

Review

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A review on CO oxidation, methanol synthesis, and propylene epoxidation over supported gold catalysts

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Abstract: The aim of this general review is to give an overview of the reaction pathways involving the transformation of carbon monoxide (CO), methanol synthesis and propylene epoxidation using gold (Au) and gold supported clusters. Over the catalyst system of Nano-gold (Au/SiO₂), the process of methane to methanol was also highlighted. A reaction mechanism proposed, indicated that molecular oxygen was consumed in the oxidation–reduction cycle. Consequently, methane oxidation to methanol can be achieved as a green chemical process. The system can also be used in other green chemical processes of liquid phase or gas phase oxidations. Methanol is expected to be a potential solution to the partial deployment of fossil source-based economies. Moreover, it is a recognized energy carrier that is better than other alternatives in terms of transportation, storage and reuse. New or improved catalysts for methanol production are likely to be discovered in the near future.

Keywords: Gold; gold-supported oxide; clusters; oxidation; methanol synthesis; epoxidation.

1 Introduction

For some time, Gold (Au) was regarded as a poorly active catalyst. Theoretical findings newly describe reason

behind the glossiness of Au surface when adsorbed by hydrogen (H₂) [1]. Nonetheless, by depositing Au nanoparticles on metal oxides through co-precipitation as well as deposition-precipitation (DP) techniques, the Au nanoparticles (NPs) displayed a high catalytic activity for oxidation of carbon monoxide (CO) at a temperature as low as 200K [2,3]. Numerous scientists and related field were motivated by this findings to probe Au catalysis several years back (1990s). The new shift in the cost of Au (US\$ 9/g) in commercial system with regards to Palladium/Platinum (Pd/Pt) (US\$ 14/g), which can propel market improvement of Au based catalysts along with economic advantage. Fig. 1 shows a reasonable increase in the annual number of articles in research that are related to catalysis of Au in previous decade especially very rapidly from 1997. A citation database service, “The Web of Science”, provided by Institute for Scientific Information (ISI, <http://www.isinet.com/isi>), has been used to search through key words such as ‘Au’, ‘catalysis’, ‘catalyst(s)’, ‘catalytic(al)’, ‘catalytically’ together with verb conjugations such as, ‘catalyze/catalyse’, electrocatalysis, photocatalysis, autocatalysis all inclusive. The articles that contain at least one of these words in the title, abstract and key word lists are automatically counted in the numbers, which therefore include a few research works that do not really cover Au catalysis.

Au Nano particles display good reactivity in CO oxidation at low temperature [4], which results to the utilization of Au/oxide accompanied by inverse oxide/Au catalysts studied widely in dissimilar reactions [5]. The mechanism of metal oxides support for Au catalyst in reactions involving the oxidation of CO is quite complex (as established by some current studies on catalyst), this is due to a lot of factors that controls the reaction of the Au-based catalyst, similar to the low-coordinated sites of a very tiny particles surface that are present [6], the nature of the support [7], the technique used to produce the catalyst [8], and the reaction conditions, etc. Even though the complexity of the nature of interface between Au and

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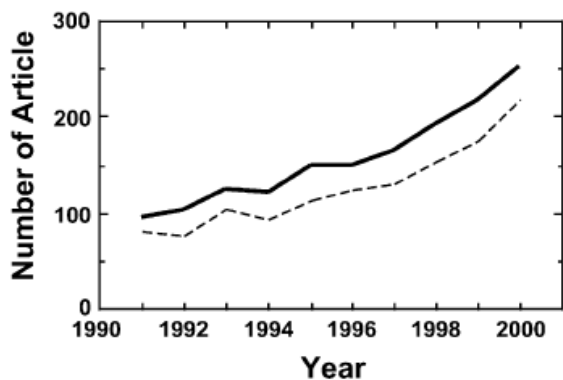


Figure 1: The numbers of articles concerning Au catalysts in the last decade. Fundamental/broaden search are represented by the dots/ thick lines separately

its support is not well understood, yet, it can have effect on the nature of active sites in reactions related to oxidation of CO [9]. Current advances regarding growth in the field of Au catalysts probing oxidation of CO are presented in few excellent reviews [7, 10]. Au catalysts supported on metal oxides, like Iron oxide (Fe_2O_3), Cerium oxide (CeO_2), and Titanium oxide (TiO_2) were examined because of their direct participation in reaction mechanism of CO oxidation accompanied by their ability to adsorb or store oxygen (O_2) at low temperatures, lattice O_2 mobility, stabilization of Au nanoparticles through means of inducing stronger interaction between metal-support, and/or to generate ionic Au species [11]. However, sadly, actual surface area of Au-based catalysts with reducible oxides as support is small compared to other catalyst with mixed oxides as support [12]. The activity of Au catalyst is highly influenced by [13, 14]: (i) The size and shape of Au particles; (ii) the methods used to synthesize the catalyst (iii) The nature of support materials (iv) The reaction taking place at the interface between Au and the support (v) And the oxidation state(s) of Au in the synthesized catalysts as reported by many studies. As a result, diverse process of absorbing nanoparticles of Au on distinct metal oxides were demonstrated by various findings, these includes; oxides of Ti, Fe, Ce, Mg and Si etc. as already reported by different research groups to overcome this problem [15]. Depending on the type of support, Au-based catalysts are synthesized through the following methods: Deposition-precipitation method, Co-precipitation, Colloidal dispersion and liquid-phase grafting method etc as previously mentioned. But deposition-precipitation (DP) happens to be the most widespread approach that is generally employed in the synthesis of Au-based catalyst with metal oxides as it support with elevated Isoelectric point (IEP), which is illustrated in the synthesis of

the oxides of Ti, Fe, Al and Ce etc. using deposition-precipitation method [16]. Recently, much attention has been drawn towards Au catalyst because of its prospective usefulness in quite a number of reactions which are vital to environment as well as industry. Current study points out latest advances on catalysis research of Au. CO oxidation mechanistic topics are summarized, focusing on Au/ TiO_2 , Au/ CeO_2 and Au/ SiO_2 together with other advances that specialize on Au and catalytic reactions of Au supported Nano-clusters [5]. Furthermore, recent developments are presented in propylene epoxidation and synthesis of methanol (CH_3OH). Perimeter interface between Au particles as well as the support plays a vital role as a unique reaction site for reactants adsorbed separately on both Au and the support respectively.

Although it is a general agreement that the role of support in Au-supported catalyst is given thus; to stabilize active Au particles, the support material interaction with Au particles is vital in catalytic activity [17]. Given an instance; oxidation of CO, exceptionally high activities have been described for reducible metal oxide support such as TiO_2 , Fe_2O_3 , CeO_2 suggesting that the support supplies oxygen to form active oxide Au sites [18], it was further suggested that the sites on Au-support interface are responsible for CO oxidation activity [19]. With these report in mind, assumption can be made to show that the most vital factor for the formation of the activity of Au catalyst which includes study of the oxidation of CO in relation to Au catalyst support on metal oxide compare to other numerous supports with different properties is the contact structure. Theoretical findings contribute to quite a number of reviews regarding Au catalytic system which is now common [20]. Shell closing provides the basis for the synthesis of Nano catalyst by describing how ligand protected clusters are produced and the reaction of clusters with definite sizes. Currently, structures like planar model are used to examine Au technique along with understanding it surface structures [21]. Electron spectroscopy (ES), High-resolution electron loss spectroscopy (HES), infrared spectroscopy (IR), small angle X-ray scattering etc. have been especially useful.

Nano sized Au particles are synthesized conveniently for experimental utilizations in solution and on surfaces. Lately, the most widespread approach of obtaining supported Au catalysts is to use supports (metal-oxides). Heterogeneous catalysis by Au has improved so greatly, Au has a reasonable catalytic activity during oxidation of CO especially with small intensity of temperature as expressed by Haruta in his previous work especially when this catalyst is spread on base metal oxide with nanoparticles as small as 5nm in size. Same activity range

is displayed by this catalyst in a broad reaction pattern which is most notable in oxygen molecule reactions. Highly dispersed Au nanoparticles support on transition-metal oxides can catalyze low-temperature oxidation of molecular CO efficiently. Several factors control the activity of those catalysts, especially size of the metal cluster, the ability of the support to supply oxygen during the reaction, and excess electrons at metal/oxide interface which determines Au atoms oxidation state. Reducible oxides represent very active catalytic supports, and among them are TiO_2 , SiO_2 , and CeO_2 among others as reported in this work [22].

There are various reports on Au NPs supported on different oxides, a few of these reports are explained in this review which gives an account on the selectivity and activity of Au catalyst and some of their reaction mechanisms in the presence of Au NPs etc. Sandoval A. et al work on Au NPs supported on various oxides such as Al_2O_3 , SiO_2 , TiO_2 and CeO_2 (reducible and non-reducible oxides) as catalysts for the WGS reaction. Their report shows a very high activity displayed by these catalysts when Au is supported on TiO_2 and CeO_2 as support that is, Au/TiO_2 and Au/CeO_2 shows higher activity than when Au is supported on SiO_2 (that is Au/SiO_2), in other words, the reducible oxides (TiO_2 and CeO_2) exhibit higher catalytic activity than the non-reducible oxides (SiO_2 and Al_2O_3) at temperature below 200°C . The catalytic activity is in this order; $\text{TiO}_2 > \text{CeO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2$. Based on this report, reducible oxides are catalytically activity compared with non-reducible oxides. [23]

Another report is based on the work of Masoud N. et al, they compare the stability of Au/SiO_2 with that of Au/TiO_2 catalyst for the selective hydrogenation of butadiene, they give a report on the activity, selectivity, and stability of 2–4 nm Au NPs catalysts, supported on either TiO_2 or SiO_2 , for the hydrogenation of 0.3% butadiene in the presence of 30% propene. They were able to compare the stability of the Au catalysts because they were prepared using same approach but on different supports. At full conversion of butadiene, only 0.1% of the propene was converted for both supported catalysts, demonstrating their high selectivity. A steady loss of activity was shown by TiO_2 supported catalysts, which was recovered by heating in air. According to this report, it was shown that the deactivation was not caused by significant metal particle growth or the strong interaction between the metal–support, but instead, it is related to the deposition of carbonaceous species under reaction conditions. In contrast, all the SiO_2 supported catalysts were highly stable, with very limited formation of carbonaceous deposits. It shows that SiO_2 supported catalysts, despite their 2–3 times lower initial activities,

clearly outperform TiO_2 supported catalysts within a day of run time. The report from this work shows that, SiO_2 support (being a reducible oxides) is highly stable with very limited formation of carbonaceous deposit, despite its lower activity when compared with a reducible TiO_2 (being a reducible oxide) which exhibit low stability. On the basis of stability SiO_2 has higher stability than TiO_2 , while based on activity TiO_2 shows higher activity. [24].

A recent work in 2018 reported by Ziyauddin S. et al on Silica-Supported Au Nano catalyst for CO Oxidation, also expressed that the catalytic activity of Au NPs supported on reducible metal oxides such TiO_2 , CeO_2 , Fe_2O_3 , Co_3O_4 is very high compared to the activity of SiO_2 being a non-reducible oxide, but silica is however an inert, inexpensive, and convenient support that can be shaped into a lot of attractive and varied morphologies. This work also gave a hint on the particle size of the catalyst, Au NPs with dimensions less than 5 nm were found to be active for a number of oxygen transfer reactions, particularly for low-temperature CO oxidation. Au clusters in the 2–5 nm range shows a very high activity, these Au NPs can have a strong interaction with the support and electron relocation may happen within either direction. Silica-supported Au Nano catalyst has become a good topic of research for CO oxidation; although, several challenges lie ahead which requires the improvement of silica-supported gold Nano catalyst filling the main necessities of any catalyst such as easy and low-cost synthesis method, high activity, selectivity, and greater stability at lower temperature. Moreover, the proof of identity for the active gold species is still a challenging job for CO oxidation reactions catalyzed by gold [25]. Although not much report have been given on CeO_2 due to limited work done on CeO_2 as a support oxide, yet CeO_2 has been reported as a reducible catalyst with a very high catalytic activity for CO oxidation, but more work needs to be done to improve the activity of non-reducible support catalyst especially SiO_2 been the cheapest, more inert and more convenient support capable of being shaped into different morphology. There is more report on the Au/TiO_2 and Au/SiO_2 catalyst.

Jürgen Behm and Daniel Widmann work on active oxygen on Au/TiO_2 catalyst, and gave account on the reaction mechanism of Au/TiO_2 and also present an important step towards the understanding of the mechanism of CO oxidation reaction on oxide-supported Au catalysts in general. Their report shows that the active oxygen for CO oxidation on Au/TiO_2 catalyst is a highly stable oxygen species, whose formation is facile and hardly activated and they proposed the species to be surface lattice oxygen at the perimeter of Au/TiO_2 interface that is activated by the presence of Au NPs.

They were able to draw some conclusion on the nature of the active oxygen from the experimental result, thus; the active oxygen species exhibit high stability that is compatible with molecularly adsorbed oxygen. And they therefore, propose that the active oxygen species is an atomic species, Au NPs have two roles in the CO oxidation reaction: First, they accumulate adsorbed CO, and second, they activate surface lattice oxygen at the Au-TiO₂ perimeter sites. In the absence of Au NPs, surface oxygen is not reactive under “normal” reaction conditions. The above conclusion results in a mechanism for CO oxidation on Au/TiO₂ catalyst at less than 80°C demonstrated in the below figure. And involves: CO adsorption on Au NPs, reaction with activated surface lattice oxygen species at the perimeter of the Au-TiO₂ interface (interface sites), and replenishment of these sites by dissociative adsorption of O₂ at them.

Rodolfo Zanell et al gave a report few years back on the methods for preparation of Au on support oxide, they prepare Au/TiO₂ using different methods; Deposition-precipitation with NaOH, Incipient Wetness Impregnation, Anion Adsorption, Cation Adsorption, Deposition-Precipitation with Urea. Using TEM they obtained the image of the calcined sample. Comparison of the results obtained by DP NaOH and DP urea shows that the DP urea is a promising method of preparation. According to the report on this work, DP by Urea will serve a better option than DP by NaOH. DP method in general is more advantageous than the other methods mentioned [27]. Although, DP method is the most commonly used approach for metal oxide catalyst support preparation, a recent report on the method of preparation of support metal catalyst as employed by different research was demonstrated by Bahareh A. et al. in their work, they compare the efficacy of the various methods to synthesize supported metal catalysts, they surveyed over 1500 literature articles from the past 3 years. They employed Pt catalysts over (SiO₂), (Al₂O₃), (TiO₂), and carbon (C) supports as examples. They gave a report on strong electrostatic adsorption (SEA) method, its latest version and charge-enhanced dry impregnation (CEDI) method. They compared and contrast these methods to those most prevalent in the literature. SEA and CEDI yield ultra-small nanoparticles, usually less than 1.5 nm average particle size, and are simple and scalable, especially CEDI, which is a simple adaptation of common incipient wetness impregnation. These methods can be extended to the synthesis of supported bimetallic nanoparticles with equally efficacious results. The report on this work shows that SEA and CEDI opens a new and a promising approach for support metal catalyst preparation [28].

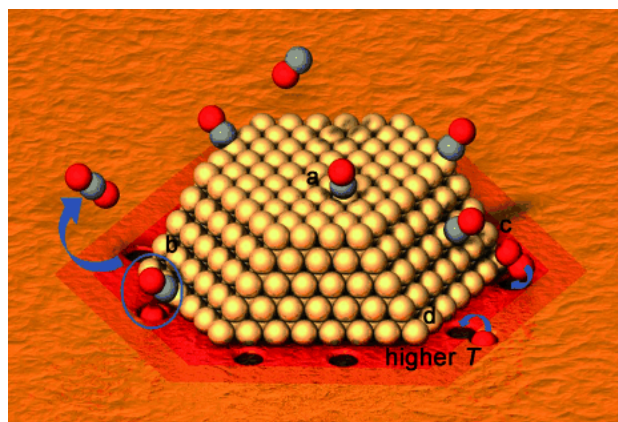


Figure 2: Schematic description of the pathway for CO oxidation on Au/TiO₂ catalysts at temperature less than 80 °C involving the above. [26]

1.1 CO oxidation

Oxidation of CO to Carbon dioxide (CO₂) has drawn much attention in Au catalyst research especially at low temperature. Oxides of Nickel (Ni), Cobalt (Co), and Iron (Fe) have been used to support Au during early discovery of Au catalyst activity for CO oxidation. [29], previously, several studies were carried out on Au catalyst over different support, however, these supports are independently inactive, but generate reasonable activity for oxidation of CO when combined together [30]. Numerous elements like; size or proportion of Au catalyst, type and nature of the support, production technique, all influence the catalyst [31]. Some literature reports that the activity of CO oxidation results from the distinction in Au [32], while others reports that the active sites results from ionic Au [33]. While other researchers maintain that catalyst activity is necessary due to both ionic/metallic Au altogether [34]. CO Oxidation is a typical reaction in which Au catalysts are extraordinarily active at room temperature, also, much more active compare to other noble metal catalysts at temperatures below 400 Kelvin. A great deal of effort is invested towards developing active catalysts for elimination of trace CO via oxidation. Previously, supported Pt/Pd catalysts were extensively probed for reaction involving CO oxidation. Haruta et al in their latest report described the reason for the high catalytic activity of Au in CO oxidation to be as a result of its high spreading. Early work of Haruta/co-workers [T.V. Choudhary et al] motivates many researchers in Au catalyst research field, hence this result to quite a number of articles touching various angles of Au catalysts, its reactions and use in the oxidation of CO [35].

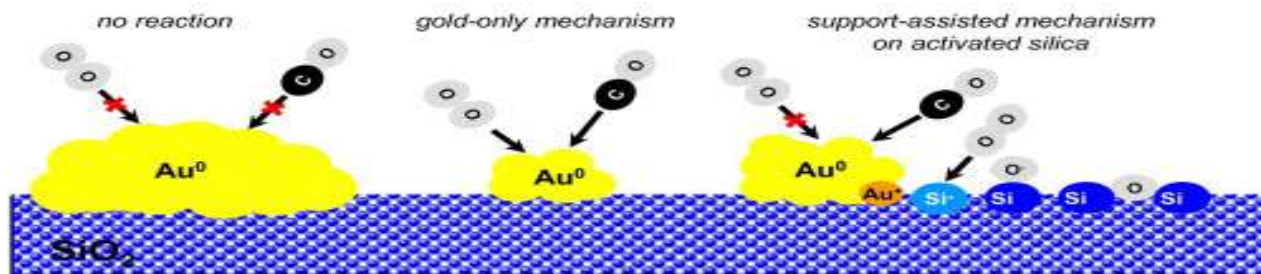


Figure 3: Schematic representation of oxidation of CO on gold nanoparticles

Haruta report Au Nano particles (NPs) as very active for oxidation of CO [36]. The two main applications of catalyst based on Au-nanoparticles for oxidation reactions of CO are: (i) The oxidation of CO in catalytic exhausts: cold start of engine is accountable for about 80% of pollution caused by powered vehicles also a big cause of pollution in the air. Au NPs play a vital role to reduce pollution emanating from vehicle exhaust. (ii) Hydrogen Purification for application in fuel cell: CO formed in reforming of methanol adversely affects Pt electrodes of fuel cell. Nanoparticles of gold have the capacity to keep down contamination of Pt anodes caused by CO. Au Nano particles supported on transition metal oxides serve as active catalysts for oxidation reactions at low temperatures [37]. The smaller the size of Au particles, the more reactive they are, and vice versa. As a result of the less activeness of exposed Au, the vitality of oxide support cannot be over emphasized. Incomplete movement of electrons can exist between metal/support from weak center. Because of this, more charge density will be achieved by the cluster thereby triggering the bond connecting molecules of oxygen adsorbed on the surface of the metal cluster [38]. Activation weakens oxygen to oxygen (O-O) bond hence, lowers the barrier so that reaction can occur with CO followed by subsequent CO_2 formation [39]. CO oxidation mechanism of Au is affected by several factors such as Au oxidation state, effect of quantum size, [40] support induced strain [41] etc.

Factors listed above points out the significance of nanoparticles of Au in CO oxidation. But the most vital points are

- (i) How to allocate shape/size to the real samples shown
- (ii) Difficulty in picturing nanoparticles with size smaller than one nanometer
- (iii) Activity of given catalyst can be exhibited by some few nanoparticles alone

In last decade, it was expressed that the existence of bilayer clusters align with the remarkable activity of catalyst for carbon monoxide, especially those clusters having just ten Au atoms whose diameter is half of one [42]. This further indicates that the structure of bilayer Au to be an evaluative property of nanoparticles of Au catalyst that is active, but have low coordinated area, particle support, effects of the movement of charge, and quantum size effects. Several proposed mechanisms exist for reaction involving oxidation of CO. these are predominantly categorized as; mechanism of nanoparticles of Au with CO without support, mechanism of Au nanoparticles with support [43]. Many factors such as kinetics, study of temperature range, kinetic isotope effect reinforce these mechanisms [44]. Fig.3. is a schematically representation of CO oxidation mechanism

Figure 4 shows growing trend in some number of publications per year involving oxidation of CO employing catalysts based on Au. Au catalyst have attracted much attention in the past years leading to numerous paper work in Au research area especially work that pertains Au catalyst in quote and CO oxidation. Showing how vital Au catalyst process is in heterogeneous catalysis.

1.2 Epoxidation of Propylene

The attention of chemical industries and research sector has been drowned over the years towards the characteristic features of Au catalyst supported on metal oxides [45]. Propylene oxide (PO) is one of the important bulk chemicals, which is used for producing polyurethane and polyols. Catalysts of Au capable of synthesizing propylene oxide in just a phase of reaction with only H_2O as byproduct have the potentials of taking the place of these approaches. Direct epoxidation of propylene for Au catalysts involves four important factors. First one is method of preparing catalyst. As evidenced in Fig 5,

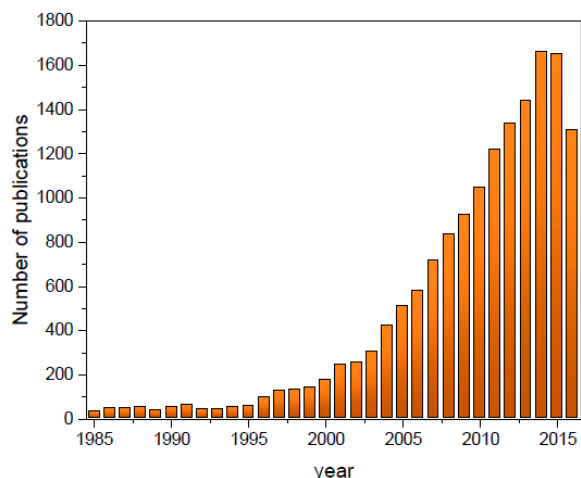


Figure 4: Number of published papers from 1985 in the Scopus Scholar database searching for both gold catalysts /CO oxidation in quote respectively (September 2016)

deposition-precipitation approach gives good selectivity above 90% resulting from epoxidation, on the contrary, impregnation fails to give any selectivity instead it oxidizes totally to CO_2 and H_2O [46]. A major dissimilarities in fine structure of the Au/ TiO_2 catalysts is that in case of impregnation, a big (several tens nm in diameter) spherical Au particle is simply mixed with smaller TiO_2 particles, whereas in case of deposition-precipitation, small hemispherical Au particles are actively contacted with TiO_2 particle at their flat planes. The factor responsible for the existence of much interval of circumference interface that is much needed for epoxidation of propylene is the link between particles of Au with TiO_2 . Secondly, the appropriate selection of the support materials, among single metal oxides, only TiO_2 makes Au selective for reaction. Furthermore, crystalline structure of TiO_2 should be anatase but not rutile and amorphous [46]. Much kind of titanium silicates, titanium supported on silicon oxide, was evaluated as Au particles support [47-52]. Using Ti placed on Si as Au supporting materials, Au becomes selective to epoxidation at temperature of about 473 kelvin, giving a good conversion rate of close to 5% [49, 54]. Hydrogen peroxide is formed on the surfaces of Au which is modified to OOH on Ti^{4+} tetrahedrally coordinated in SiO_2 matrices to react with propylene as presented by a reaction pathway [53, 54]. Among titanosilicates such like TS-1, Ti-zeolite, Ti-MCM41, Ti-MCM48, having dissimilar pores sizes and structures; Ti-MCM48 is proved to give the leading catalytic achievement [54]. When Ti/Si exceeds 3/100, TiO_2 species are assembled to yield CO_2 at temperatures above 373 K. This upper limit on Ti/Si ratio is also valid to Ti deposited on SiO_2 . SiO_2 supports were also

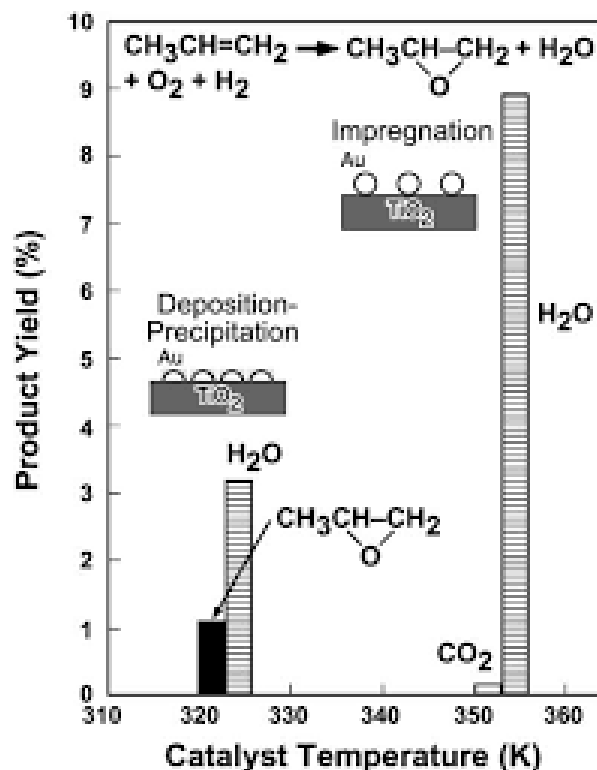


Figure 5: Epoxidation of propylene over Au/ TiO_2 prepared by different methods [46].

tested with a variety of specific surface area from $60 \text{ m}^2/\text{g}$ (non-porous) to $800 \text{ m}^2/\text{g}$ [50]. It appears that there is an optimum pore size, its distribution, and specific surface area. The third one is the size of Au particles. Decrease in size of particles of Au favors hydrogenation of propylene to propene [55]. This phenomenon has been confirmed by several researchers [53]. The fourth is the additives.

When titanium silicates are used as a support and Au is deposited by deposition-precipitation, complete washing to remove sodium (Na) and chlorine (Cl) causes the propynaldehyde formation instead of PO; however, easy filtration of Au hydroxide precursor results to selective PO with no more cleaning [47]. This result strongly indicates that alkaline and/or chloride may play an important role in the selective epoxidation. It has been claimed that many alkaline and alkaline earth chlorides work as a good promoter [45, 49]. However, the optimum amount and sites and the mechanistic role have not yet been understood. Successive alteration of the activity of Au catalysts at every hour is one out of the numerous challenges which require solution in the development of direct gas-phase epoxidation of propylene. This is because of acidic/oligomerized species slightly assembled on the surface of catalyst [53, 54]. Even without any substantial buildup in Au particles size, it is difficult to re-impose the

early activity entirely regardless of heating temperature to burn off the hydrocarbon residues. Through elementary research, Goodman et al employ Au (1 1 1, 1 0 0) for propylene uptake [56]. During the formation of PO, no selectivity was shown by oxygen when it was absorbed onto even surfaces of Au.

1.3 Methanol Synthesis

Methanol (CH_3OH) is operated broadly as a crucial compound and a basic item in the manufacture of synthetic hydrocarbons, solvent, energy storage medium, and fuel. This status is expected to last in the near future or even improve to the point of making this compound a central participant in worldwide economic landscape. Based on these reasons, every improvement to its manufacturing process, as regards to energy savings, optimization, etc., has potential to promote relevant economic benefits. There are 3 fundamental ways through which CH_3OH can be made, these include; first syngas production, secondly is to process CH_3OH while lastly is subsequent detachment. Beneficial idea in postulation of renewable energy which will aid in overcoming inherent variation in supply of renewable energy requires conversion of excess electrical energy storage in form of chemical energy. CH_3OH being a storage molecule particularly draws attention, due to storage and transportation ease. It is possible to use CH_3OH as a source of CO_2 , neutral synthetic fuel or a feedstock for synthesis of a variety of basic material. Nowadays, CH_3OH is largely obtained from syngas containing CO, CO_2 and H_2 , which is obtained through catalytic reforming of fossil fuels [57]. Nonetheless, through replacement of fossil fuels as carbon source with anthropogenic CO_2 obtained through industrial exhaust or coal power plants [58, 59], for instance, so called “green CH_3OH ” can be obtained [60, 61]. It is possible to reduce total emission of CO_2 through this means [59]. This process was first applied by technical means in ‘Emission-to-Liquid’ (ETL) technology developed by Carbon Recycling International (CRI), which since 2011 is still in use with a manufacturing record of about 5 mil volume per liters annually [62]. In industrial CH_3OH production from CO_2 -enriched syngas typically Cu/ZnO+MeOx catalysts are employed [57]. These have been optimized to a very high performance level under industrial relevant reaction conditions (at elevated temperatures and pressures) because synthesis of industrial CH_3OH is of immense importance [63]. Based on opinion, it can be regarded as better use for hydrogenation of CO_2 for the above operation. On the contrary, manufacture of CH_3OH from CO_2 is ordinarily preceded through

unpleasant making of CO through means of reverse water-gas shift reaction [64, 65]. Consequently, apart from the high rate of manufacture of CH_3OH , a principal element which needs to be put into consideration is the selectivity towards manufacture of CH_3OH . Hitherto, the catalytic system studied is very scarce, presenting little or no activeness for manufacture of CO in CO_2/H_2 gas reaction mixtures for manufacture of CH_3OH , for example, differently promoted Cu-based catalysts [66], Au catalyst supported on 3ZnOZrO_2 and Ag catalyst supported on 3ZnOZrO_2 respectively [67], carbon nanotubes supported Pd-ZnO catalyst [68]. Cu-based catalysts is active when used in reverse water-gas shift (RWGS) reaction between 230/260 °C especially on commercial basis, which led to manufacture of immense quantity of CO besides methanol, and consequently, low selectivity concerning methanol [68]. It is especially true for Au catalyst support on zinc oxide (ZnO). At present, the much higher price of Au in comparison with CO_2 hydrogenation to CH_3OH support on Au catalysts is economically not competitive, but these previous reports clearly demonstrated their promising abilities for certain utilization, e.g., small scale processing under dynamic operation conditions, as expected by principles of renewable energy [69]. Discerning the basis of high activity/selectivity of Au catalyst supported on ZnO in order to hydrogenate CO_2 into CH_3OH is so captivating especially from the principles of sciences. Here, it is worth stating for both Au- and Cu-based catalysts the existence of Zn species seems to be mandatory so as to attain high CH_3OH formation rates as well as selectivity [70]. This suggests that Au/ZnO and Cu/ZnO benefit from same effect, namely ZnO_2 partial reduction under reaction conditions in highly reductive atmosphere with subsequent migration of ZnOx surface species on nanoparticles of Au or Copper (Cu), leading to either formation of AuZn or CuZn alloy, or of ZnOx shell [71]. Meantime development of Cu catalyst and the role played by this catalyst in mechanism of oxides of carbon especially CO_2 along with CO hydrogenation reaction to CH_3OH is being displayed by previous studies [72], but no adequate knowledge corresponding to Au catalysts supported on ZnO is available [69]. This kind of outcome can be pictured on the surface of Au consequently showing the reason why Au catalyst support on ZnO has better regards toward the production of CH_3OH from CO_2 and H_2 in comparison to other metal oxide support on Au catalysts [69]. Interestingly, Martin et al recently demonstrate the promotion of Cu-ZnO- Al_2O_3 catalysts for CH_3OH formation through addition of Au, as explained through stabilization of metallic CuO species in close region to ZnOx. [66]

2 CO oxidation reaction

Generally speaking, reactions involving oxidation catalysis usually requires use of transition metals such like Au, Pd, Pt, Ir, Rh, etc. with a metal oxide support such as TiO_2 , SiO_2 , CeO_2 , Fe_2O_3 , PtO_2 etc. Various researchers have worked on the oxidation of CO especially the catalytic activity on metal clusters surfaces [73, 74]. Starting from Langmuir's work on Pt wires as a noble metal [75]. Such reaction involves simple molecular rearrangements that make it attractive to probe fundamental concepts in catalysis. CO oxidation also remains some of the good and standard instances showing lack of change in structure; the degree of turnover does not depend on metal dispersion, notwithstanding the fact that unprotected metal atoms are not the same with clusters that possess different size especially in term of structure and coordinative unsaturation

2.1 Oxidation by Au/ TiO_2

Oxidation of CO is a distinctive reaction by which Au catalysts are extraordinarily active at room temperature even much more active than other noble metal catalysts also at temperatures less than 400 Kelvin. Most intensively studied for this reaction is Au support on TiO_2 . This is because neither Au nor TiO_2 alone is active for oxidation of CO instead their combination generates remarkably high catalytic activity. CO oxidation mechanism is one of the focuses in recent catalysis research work [76-78]. Active site of Au catalysts accommodates particles of Au in metal form indicating 2112 cm^{-1} absorption band for CO, on the contrary, all manner of Au oxides showing 2151 cm^{-1} Au species absorption band for the CO mentioned earlier does not account for rise in activity of the catalyst under stable position [79, 80]. However, smooth surfaces of metallic Au do not adsorb CO at room temperature [80], indicating that CO is adsorbed only at steps, edges, and corner sites. Thus, smaller metallic Au particles are preferable [81]. Au catalyst support on Ti was employed as sample and an encouraging outcome obtained from it based on the work of Goodman et al which is presented in the below figure 5, the turn over frequency for oxidation of CO reaches extreme at a diameter of Au islands of 3.5 nm (3 atoms thick) at which Au relatively loses its metallic nature [82]. They propose that this change might correspond to high catalytic activity. Since adsorption of CO on oxide Au sites is inhibited by moisture because of stronger adsorption of H_2O molecule [83], activity enhancement strongly suggests that metallic Au particles are indispensable for adsorption of CO.

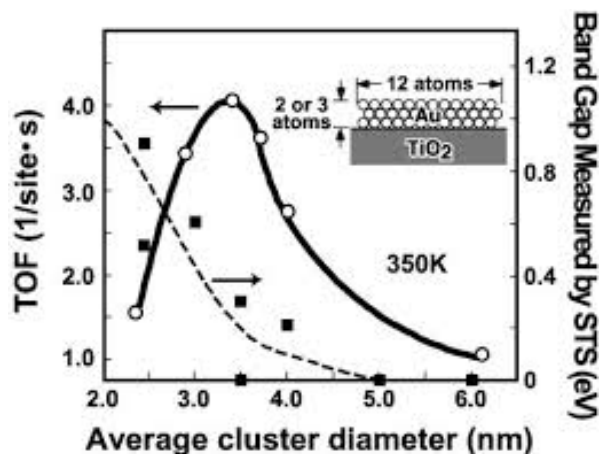


Figure 6: Turn over frequencies/band-gap measured by STM as a function of the diameter of Au islands deposited on TiO_2 [76]

The strong contact existing between Au particles and TiO_2 support is absolutely necessary for extraordinarily high catalytic activity, because periphery sites are assumed to act as sites for reaction of CO adsorbed on Au with oxygen adsorbed on support. Baiker and coworkers make Au/ TiO_2 and Au/ ZrO_2 by immobilizing Au colloids of about 2 nm size on TiO_2 and ZrO_2 and indicate that strong interfacial contact between Au and oxides was not necessary [84]. Nevertheless, their observation of enhancement of activity by heating catalyst samples in reactant stream at 423 K or calcination in argon at 673 K indicates the contribution of strong contact. It was later reported that Au/ TiO_2 interface was important for oxygen activation [85]. Experiment by S. Tsubota et. al obviously signifies rise in calcination temperature yielding a rise in the activity of catalyst emerging from blending powdery form of TiO_2 and Au colloid, notwithstanding Au particles becomes large [86]. On the contrary, there is rise in the activity of catalyst emerging from great amount of steps, edges, corners of particles of Au relating to CO oxidation; along with how the support relates with the catalyst also contributes to an additional rise in activity at least by one order of magnitude [87]. Overall mechanism of reaction expressing the catalytic operation of Au catalyst supported on TiO_2 on vast temperature region was expressed by M. Haruta et al. [88]. Arrhenius plot in Fig. 7 implies three temperature regions with distinct rates of kinetics at visible energies of activation.

Furthermore, the activation energy for the step, corner, sites and edge, is seen almost at 0 kJ/mol. It means when Au particles are small enough, catalytic activity may be detected at any temperature. Actually unsupported Au powder (30 nm in diameter) exhibits measurable activity for oxidation of CO at 200 Kelvin with noticeable

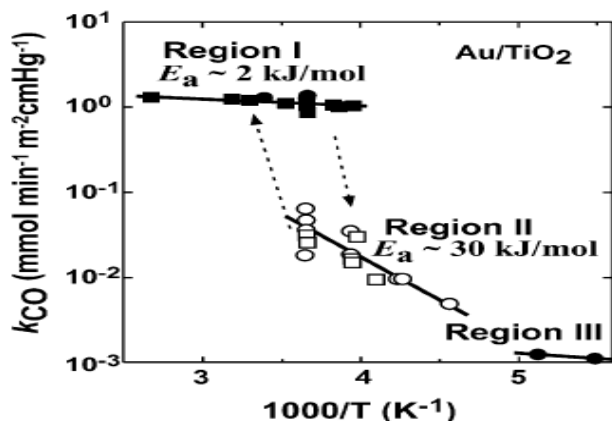


Figure 7: Arrhenius plots for CO oxidation over Au/TiO₂ catalyst [84]

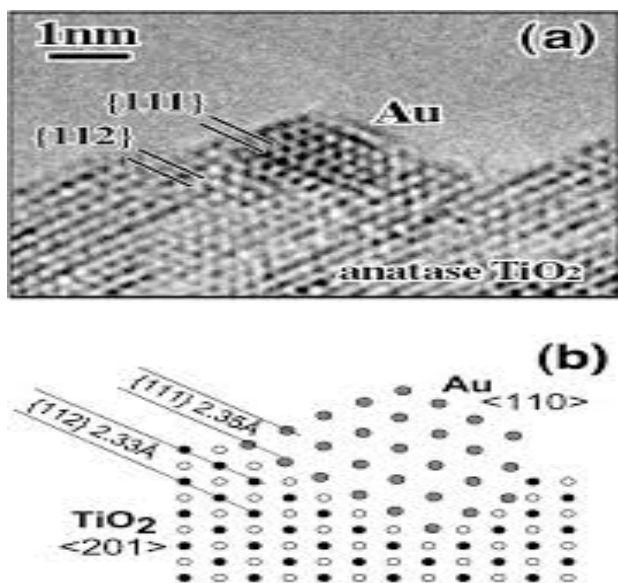


Figure 8: (a) Transmission electron micrograph for Au/TiO₂ contact interface and (b) its schematic diagram [84]

energy of activation of nearly zero [87]. In addition to above report, a few other interesting features of Au/TiO₂ catalysts were described by using model catalysts [78] and by high resolution transmission electron microscopy [78, 89, and 90]. Fig. 8 shows typical epitaxial structure of Au with its support contact [89]. The empty space connecting particles of TiO₂ pictured additional particles of Au in the process of conversion of the metal to its oxides at reasonable temperatures.

Adsorption of CO on Au surfaces is one of the important steps in oxidation of CO. Boccuzzi et al. have found that Au/TiO₂ catalyst prepared by deposition-precipitation method contains three different Au sites for CO adsorption depending on conditions of pretreatment [83]. Adsorption of CO at successive sites of Au metal

(2110–2120 cm⁻¹) subsequent to heating of the Au metal in the presence of air at increased temperature, adsorption of CO on Au oxide (2176 cm⁻¹) showing much oxidation and hydration, and successive /crossed-bonded adsorption of CO in contact with tiny clusters of Au (2050–1900 cm⁻¹) brought about through disturbances caused through the formation of negative charge on support reduction by H₂. The study of the adsorption of CO and oxygen over Au/TiO₂ employing fixed bed flow reactor equipped with mass spectroscopy has shown that CO and O₂ adsorption takes place promptly, and the production of CO₂ rises pending on when saturation is achieved through adsorption of oxygen on perimeter sites being reduced [91]. Moreover, moisture also enhances oxidation of CO over Au/TiO₂. Catalytic activity is so low under dry condition (0.1 ppm H₂O) than under the ordinary experimental condition (about 3 ppm H₂O) [92].

2.1.1 Oxidation by Au/CeO₂

Oxidation of CO catalyzed by Au atoms supported by dissimilar oxides was addressed through several theoretical studies [93], oxidation has been modeled in the presence of oxygen ad species yielding to formation of surface CO-O intermediate complexes that leads to oxidation of CO with CO₂ desorption. Au-based catalysts Activity towards oxidation of CO is known to be sensitive to (i) method of preparation; (ii) nature of supports; (iii) size of Au particles; (iv) pre-treatment conditions; and (v) Au-support interactions [94]. Among all, support choice is of primary importance. The support usually plays multiple roles, such as mechanical functionality, i.e., to disperse and stabilize supported nanoparticles against agglomeration and at same time it could participate in catalytic process. Conventionally, CO oxidation supports can be classified depending on their reducibility or ability to supply reactive oxygen: reducible materials such as CeO₂, Fe₂O₃, CoO_x, with non-reducible supports like MgO and Al₂O₃. Currently, Au support on reducible transition metal oxide always exhibits better activity for the oxidation of CO under Au support on non-reducible oxides [95]. Nevertheless, non-reducible materials having electron-rich oxygen vacancies may enhance activity of Au catalyst by activating gaseous oxygen [96]. As a result of chemical properties of ceria, it has become one of the most promising supports for oxidation reactions as it is being studied widely [97]. Relevance of CeO₂, as support for nanoparticles of Au, is mainly based on its high capacity to store oxygen which results from oxygen mobility present in its lattice [98]. The latter is

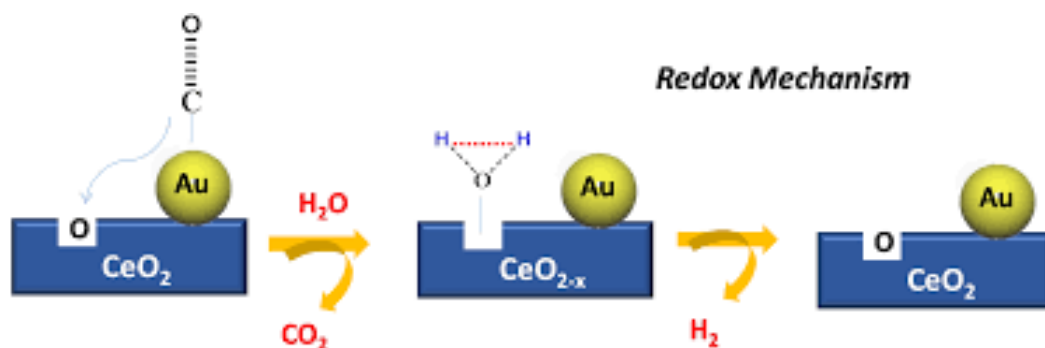


Figure 9: Simplified CO oxidation mechanism in a model Au/CeO₂ system. Oxygen vacancies of ceria on the Au/CeO₂ contact perimeter can chemisorb gaseous oxygen (O₂→O₂^{•-}) producing oxygen activated species able to react with CO molecules adsorbed on Au particles (C≡O→Au) to generate gaseous CO₂ and new oxygen vacancies [93]

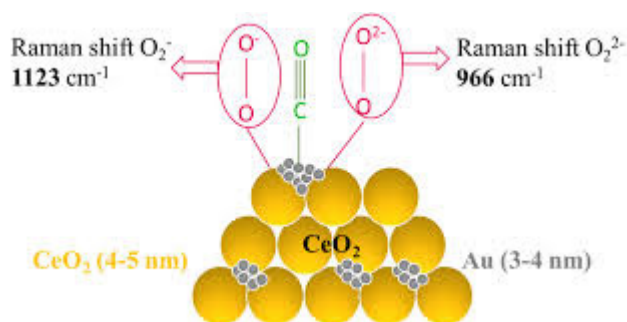


Figure 10: Schematic representation of CO oxidation catalyzed by gold on nanocrystalline reflecting the role of oxygen reactive species. (CeO₂ yellow, Au grey). The position of the characteristic Raman bands of superoxide (O₂^{•-}, 1123 cm⁻¹) and peroxide (O₂²⁻, 966 cm⁻¹) species are shown). Adapted from Guzman et al [103].

directly correlated to creation, stabilization, with oxygen vacancies diffusion, especially on oxide surfaces, as a result of reversible redox behavior of Ce⁴⁺/Ce³⁺ couple hence, resulting in the formation of non-stoichiometric oxides CeO_{2-x} (0 < x < 0.5). The concentration of these structural defects is usually correlated with catalytic activity in reactions involving CO elimination [99]. In addition, these defects may act also as an activation point of CO and O₂ molecules, facilitating reaction. Indeed, ceria participation in reaction mechanism is vital since the main criticism towards CO oxidation mechanisms involving only Au atoms is related to poor capacity of Au for oxygen chemisorption and activation [100]. Figure 9 shows a simplified reaction mechanism of CO oxidation over Au/CeO₂. Rapid Ce⁴⁺/Ce³⁺ inter-conversion leads to generation of oxygen vacancies (equation 1) where O₂ can be chemisorbed (Equation 2). In parallel, CO sits on metallic Au particles (Equation 3), leading to adsorbed CO that would further react on metal/oxide interface with O₂ activated on support vacancy producing final CO₂,

Oxygen species bonded to CeO₂ are incapacitated by Au clusters consequently promoting production of plenty reactive species according few authors [101]. In some cases, these reactive sites can participate in the reaction mechanism by creating activated species directly from the reactants mixture (e.g., peroxi-like and superoxi-like species), potentiating the oxidation reactions [102]. Guzman et al. clearly demonstrate the role of these oxygen activated species in the CO oxidation process using in situ Raman spectroscopy. They obtained Raman spectra of Au support on Nano crystalline ceria before and during the CO oxidation test, detecting bands at 1123 and 966 cm⁻¹ ascribed to superoxide and peroxide species, respectively [103]. These bands virtually disappear during CO oxidation, indicating the direct participation of these oxygen species in the reaction. The study also stated that the formation of defect sites on Nano crystalline ceria is promoted by the Au presence underlying the importance of the Au/CeO₂ contact and their synergistic effect. Figure 10 schematizes the CO oxidation process picturing the direct participation of reactive oxygen species in the process.

Given the importance of oxygen defects in Ce in order to achieve better performances in CO oxidation, there has been a research trend in last decade aiming to potentiate formation of oxygen vacancy on Ce lattice. O²⁻ removal from surface or lattice of oxide may be achieved via several methods such as thermal treatments, electron irradiation, X-rays exposition, or chemical reduction [99, 104, 105]. Nevertheless, in the case of catalytic applications, most popular strategy is to dope ceria with lower valence metallic cations [106]. Oxygen vacancies formation of CeO₂-MO_x support is directly related to formation of a Ce-M solid solution. Dopant ion can modify both the chemical properties and the structural features of ceria because of the similarities of its ionic radius and electronegativity with that of ceria and is thus regarded

as the most suitable ceria modifiers. These dopants can provoke structural distortions such as ceria lattice contraction, thus favoring formation of oxygen vacancies through mechanical stress.

In summary, Au/CeO₂-based catalysts represent an excellent option for the direct oxidation of CO in contaminated atmospheres with potential utilization in environmental catalysis. A number of factors can influence catalytic properties of this type of material, such as Au particle size, method of preparation, and Au/CeO₂ contact. However, there is general agreement on the important role played by Ce. With all other factors optimized (Nano Au particle size, metallic dispersion, etc.), highly effective CO oxidation catalysts can be produced only when ceria electronic properties and defect concentration is tailored with an adequate dopant. Vast efforts have been made in recent years aiming to achieve an optimum performance, but there is still some room for further improvements. Limited number of reports on CO oxidation by Au/CeO₂ is available; some are report from Matteo F et.al. They also report that, low-temperature oxidation of molecular CO can be efficiently catalyzed by highly dispersed Au nanoparticles support on transition-metal oxides. Also, according to this report, catalysts activity is controlled by many factors, most notably is, the size of metal cluster, ability of support to supply O₂ during reaction with excess electrons at interface of metal/oxide determining oxidation state of the Au atoms. Ceria can store oxygen therefore because of this fact it is the most efficient reducible oxides among others, as the activities of these oxides is generally elevated catalytically.

2.1.1.1 Preparation of Au/CeO₂ Catalysts

So many methods have been used to prepare Au/CeO₂ catalyst some of these methods include deposition-precipitation (DP) method that is commonly employed; Jia M L et al report the preparation of Au/CeO₂ via this method. According to this report, the support was made through preparation of an aqueous precipitate and by using ammonia with adequate amount of PEG-6000 in the various steps of the process, accompanied by treatment in micro-wave. On the other hand, the catalyst (Au) is prepared through dissolution of a suitable amount of chloroauric acid (HAuCl₄·3H₂O) in deionized water, followed by pH adjustment, addition of the support and heating. According to this report, the catalyst showed a high catalytic activity [107]. Another method is an interesting advancement like employing supercritical CO₂ in the same manner with anti-solvent engaged in Au catalyst production mostly when this catalyst

is supported on ceria [108]. The catalyst precipitates on adding the precursor solution to supercritical CO₂. Rise in activity of Au catalyst is observed when it is related with systems that are produced ordinarily or by traditional process; such conduct can be expressed as arising from change in velocity of nucleation when making the catalyst. Newly, a novel method based on the photo-thermal effect generated from localized surface Au Plasmon resonance (LSPR) has been proposed for preparing Au/CeO₂ core-shell structures [109]. Core shell structures of Au catalyst supported on ceria was achieved by way of combining ceria solution with reverse micelle Au (III) solution and solution of sodium hydroxide (NaOH) according to the findings of Mitsudome et al. [110]. Combination of the above solutions takes place giving rise to oxidation-reduction reaction of Au (zero oxidation state) along with ceria (oxidation state of IV) leading to core shell structure of Au support on CeO₂. Furthermore, utmost selectivity of alkene is acquired from the combined outcome of the above structure in partial hydrogenation reaction of diverse alkynes. Bera and Hedge [111] proposed the solution combustion method to prepare Au/CeO₂ catalysts. In this method, Au remains in ionic form until a thermal treatment at 800 °C is applied. Synthesis of Au catalyst on CeO₂ support in vapor phase was recommended by Yang et al. [112]. The above process involves annihilating the targeted metal through means of employing 2nd harmonic generation neodymium-doped yttrium aluminum garnet (Nd-YAG) laser on top of the cold plate where the oxide support is placed. This preparation method appears to be very versatile, i.e., a variety of efficient catalysts can be designed by using simple and flexible control of different synthetic parameters. Another flexible means of processing Au catalyst is to decompose a precursor from single-source [113]. According to R Reina et al, the method normally uses the double complex salts (DCS) of transition metals, ionic compounds for which cation and anion are coordination compounds, and appears so convenient in synthesizing catalysts consisting of two metals known as bimetallic. This catalyst is processed by two ways: impregnation of salts consisting of only single metal known as monometallic salt progressively on the support, other way also involve impregnation of DCS organic solution. Spreading the catalyst on supports with high surface area is another easy and frequent way of forming the catalyst as employed in previous years. Rise in dispersion of Au on the surface of support and also ratio of rise in surface to the bulk will likely occur when this approach is employed and for that reason complete Au/CeO₂ interface exposure to the reactants. The latter

effect is observed when the size of both Au and CeO₂ nanoparticles is similar. R Reina et al. [114] performed an extensive study over the deposition of bare or transition metal-doped Au/CeO₂ catalyst over alumina.

2.1.1.2 Oxidation Reactions Catalyzed by Au/CeO₂

A well-known property of large volume of metallic Au is its high inertness and non-changing character being ideal for jewelry purposes. Of all the transition metals, Au possess small chemical properties and consequently termed “least” in reaction chiefly because of its small catalytic activity [115]. On the contrary, this becomes untrue as small particles of Au at Nano level spread over a support possesses high reactivity primarily when a metallic oxide or activated carbon is used as support [116]. Among different options, ceria results frequently in an optimum choice as support for Au nanoparticles. As a result of its excellent redox features, Ce is probably the most extended support employed in oxidation catalysis, and Au/CeO₂ combinations result in a perfect synergy. Here, attention is driven to some number of reactions in that Au/CeO₂-based catalysts have an outstanding behavior. Several reports were made on the oxidation reaction catalyst by Au/CeO₂, some of which were reported at room temperature, in which case the induction period arising from unreduced cationic Au was disclosed and the effect of humidity in the reaction was investigated during induction and deactivation period. After the induction period, the deactivation phenomena of Au/CeO₂ catalyst at varied rates under both wet and dry streams were observed. In contrast, in slow and fast deactivation was made which shows a slow deactivation under dry stream, a fast deactivation in wet stream was first observed due to rapid blockage of active sites by water adsorption, followed by a slow deactivation rate due to gradual formation of surface carbonate species over catalyst with time on stream. And a mechanism was proposed to illustrate the existence of induction period under both wet and dry streams [117]. Recently, a report on the effect of Au/CeO₂ interface was given for the catalytic oxidation of CO over Au nanoparticles support on ceria Nanocrystals by Ha Hyunwoo et al were they synthesized Au nanoparticles (NPs) and modeled it through simulations using DFT calculations, thereby, providing an insights into the catalytic function of CeO₂-supported Au NPs toward CO oxidation depending on the shape of CeO₂ and ratio of CO/O₂. [118]. Fernasi M et al also gave a report on the mechanism of CO oxidation on Au/CeO₂ catalysts: Activity of Substitutional Au³⁺/Au⁺ Cations and Deactivation of Supported Au⁺ Adatoms via theoretical findings. Through their calculations, they predict that the

reactivity of Au NPs nucleated at oxygen vacancies can be recovered for cluster sizes as small as Au₂ [119]

2.1.2 Oxidation by Au/SiO₂

A lot of advances have been made in the area of Au catalysis; some of these reports are on CO oxidation by Au/SiO₂ expressed by H. Zhu. et.al according to this report, it was recorded previously that SiO₂ has been shown to be an unsuitable support for preparing Au catalysts for CO oxidation [120, 121]. Although Au support on mesoporous oxide of silicon display particles of Au that are not large if processed through co-assembly approach, yet the inactiveness inherent by this catalyst towards the oxidation of CO cannot be over emphasized. This is based on the studies of the above author [121, 122, and 123]. The reason why the supported Au catalyst is inactive is because of the fragileness of the interface at both Au and the support, and also lack of proper elimination of small pieces of this catalyst as learned from advanced research [121, 122, and 123]. We have presently observed from advance studies that this catalyst displays elevated activity towards oxidation of CO when it is formed from a precursor [124–126, 127]. The present challenge still notwithstanding cross-examines the possibility of synthesizing this catalyst support on SiO₂ in the absence of such nanopores. The effectiveness of the cross-examination proves that the above challenge can be overcome because the pore channels of the catalyst is expected to stop the particles of Au situated in the pores from developing [127, 128, 129]. More research were carried out and more emphasis made as well in employing precursor of Au support on ethylene chloride [130-133], also expressing the possibility of forming mesoporous SiO₂ with no obligation of forming active Au catalyst support on same oxide of silicon. Au support on mesoporous silicon oxide is given much scrutiny [121, 134, and 135], there is no literature work on the activity of Au catalyst and no esteemed facts concerning what will become of the particles of Au when heated at elevation temperature in converting it to oxide. These present some of the deficiencies in earlier research. Hence, further work provided a solid example that Au/fumed SiO₂ could be very active for CO oxidation.

2.1.2.1 Effect of catalyst pretreatment

Pretreatment is crucial in activation of Au/SiO₂, its importance lies in the removal of organic ligands and fragments. A careful inspection of literature indicated analogous scenarios. For instance, Au/TiO₂ catalysts have

been prepared using $\text{Au}(\text{PPh}_3)_3(\text{NO}_3)$ [134], $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$ [135], $(\text{Au})_x(\text{C}_6\text{H}_5\text{CH}_2)_2$ [136], $[\text{Au}_6(\text{PPh}_3)_6](\text{BF}_4)_2$ [137], $\text{Au}_4[(\text{p-tolyl})\text{NCN}(\text{p-tolyl})_4]$ [138], $\text{Au}_{13}[\text{PPh}_3]_4[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_4$ [139], or polymer-stabilized Au particles [140] as precursor, and others have made Au/SiO₂ using $\text{Au}(\text{PPh}_3)_3\text{Cl}$ [141] along with ligand capped nanoparticles of Au [142]. Aminosilane was charged with Au, this was expressed by Mou et al. [143]. Activity of a Catalyst is favored or will be risen when fragments/protecting ligand are eliminated during the reaction process according to the above references, but achieving this is quite challenging [144]. The same setback is also experience when using ligand-protected colloid [145]. According to the principles of chemistry of surfaces, metals having spotless surfaces have good reactivity but the activeness of such surfaces decrease when the surface is contaminated. [146]. Thus, catalyst pretreatment is very important for such types of supported Au catalysts, and pretreatment conditions should be rigorous enough to yield bare Au particles, but not so harsh that it result to very large Au particles.

2.1.2.2 Implication of post-treatment in both acid/basic medium

Activity of Au catalyst support on SiO₂ is not the same especially when handled in distinct medium (Fig. 7). Treating calcined (and activated) Au/SiO₂ in NaOH solution, followed by re-calcination promote the activity, whereas the treatment using HNO₃ vapor had a harmful effect on activity. Some researchers used ammonia (NH₃) or NaOH solutions to treat the chloride-rich Au/Al₂O₃ or Au/TiO₂ and found that the method could remove excessive chloride [147,148]. No ppm-level chloride is obtained if the contemporary means of synthesizing Au catalyst support on silicon is adapted, this should be taken into consideration [127]. Only further heating of Au catalyst on SiO₂ support in NaOH solution shows a good effect. Thus, it is speculated that the role of pretreatment in our case is to tune the surface property of the support or change the structure of the active sites. No much literature work explaining the effectiveness of the oxidation of CO₂ or even the characteristic that acid and base shares in common. As it was taken into account that Au catalyst formed in solution of base shows a rise in the activity, on the contrary, when processed in solution of acid, less activity is obtained [149,150]. Au on certain incipient metal hydroxides was more active than Au on corresponding metal oxides according to Iwasawa et al. [151]. Liquid-phase CO oxidation on Au nanotubes was significantly promoted in the presence of a basic solution than water according to Dumesic et al. [152].

Basic medium favors Pt catalyst support on the oxide of aluminum by infrared (IR) spectroscopy in the oxidation of CO; this is based on Lefferts et al. [153]. Potential capacity of acid-base characteristic in the oxidation of CO cannot be overemphasis as a matter of fact. On the other hand, reactivity of Au catalyst is influenced by it particles shape as expressed by both Haruta/Goodman [15]. Perhaps, when Au catalyst was heated and treated, it particle structure undergoes transformation.

2.2 Propylene Epoxidation

Due to the growing environmental issues in chemical synthesis and processing, there has been increasing interest in the development of new processes for minimizing pollution and reducing energy consumption. Heterogeneous catalysis plays a crucial role in this respect, since it is widely used to reduce emissions from automobiles, reduce byproducts, and improve the selectivity of important chemical products in the petrochemical as well as other chemical industries [154]. Computational and experimental investigators have been working together to better understand fundamental characteristics of a wide range of catalytic reactions. Haruta's group initially started working with Au nanoparticles supported on TiO₂, but they gradually transitioned to mesoporous titanosilicates (Ti-SiO₂) as the supports [155]. Delgass's group has focused on microporous titanosilicate supports, which demonstrate better results, even with low Au loadings [156]. Jingjing et al focus on the selective epoxidation of propylene to yield propylene oxide (PO) using heterogeneous Au-based catalysts. According to their report, they ascribed The catalytic activity of Au and Au alloy nanoparticles (a few nm in size) to various mechanisms, involving reactions occurring at neutral Au atoms that differ from bulk Au atoms (due to different degrees of coordination), quantum size effects that change the electronic structures of nanoparticles, or charge modification of Au atoms through the interaction with oxide supports [157]. This report gives a hint on propylene epoxidation of Au with various oxide support such as; Au/TiO₂, Au/CeO₂ and Au/SiO₂

2.2.1 Propylene Epoxidation Au/TiO₂

Operation of Au catalyst support on Ti in the presence of oxygen to reduce gas in propylene epoxidation to it oxide have been carried out through experiments and density functional theory calculations (DFT). It was observed that

using both H_2 and CO as co-reactants, PO can be produced. The output of PO was far lower with CO compared to H_2 . Operation of CO as co-reactant is an evidence that support oxygen were employed during processing of propylene oxide as expressed through analysis of steady-state isotopic transient kinetics [158]. Present study explores the role of co-reactants in the direct epoxidation of propene to PO on Au/TiO₂ catalysts, using experimental and theoretical tools. When The H_2 was substituted by CO as a co-reactant, PO formation was observed but with lower PO yields. PO selectivity, on the other hand, was >99% in both cases and catalyst deactivation, which is a common feature on Au/TiO₂, was also observed in the case of CO, with time on stream [158].

2.2.1.1 Reaction path way of Propylene Epoxidation Au/TiO₂

Sobolev Vladimir et al report on the mechanism of reaction of Au NPs supported on TiO₂ which was known to catalyze vapor-phase epoxidation of propylene with molecular oxygen in the presence of H₂ as the necessary reducing co reagent. Were they report the use of carbon monoxide instead of hydrogen to accomplish such reaction. The reaction mechanism which they proposed involves the formation of specific oxygen species arising from O₂ on catalytic sites reduced with CO. which is relative to the generation of highly reactive oxygen species (detectable by oxygen isotopic exchange) on the surface of Au/TiO₂ treated preliminarily with CO [159]. Recently in 2018, Ji J et al also report the reaction mechanism of direct propylene epoxidation over Au/TiO₂/SiO₂ via theoretical simulations where they produced the experimental data such as the product distributions as a function of temperature, pressure, feed composition etc. they also report on the influence of structure on the catalyst performance and the influence of close interactions the kinetics of the reaction at maximum coverage. Using this model, they identify an operating condition which helps them to control the efficiency of hydrogen of the system. Such conditions are; low reaction temperature, low hydrogen feed concentration, and a relatively high oxygen feed concentration. Their work creates a route for exploring more complex bimetallic catalysts for simultaneously achieving high selectivity and activity for the synthesis of propylene oxidation. [160]

2.2.2 Propylene Epoxidation Au/CeO₂

This reports a one-pot epoxidation of alkenes with O₂, performed with nanoparticles of Au/CeO₂ and a silylated

materials of Ti-MCM-41 with two promoters; dye and hydrocarbon, the initiator is capable of forming organo Au species which promote hydrocarbon formation (3-methylpentane, ethylbenzene, or cumene) a rise in the yield of alkene is achieved when hydro peroxides is employed in epoxidation involving Ti. The epoxidation reaction of 1-octene with molecular oxygen δPO_2 1/4 12 barsP at 90°C over azobisisobutyronitrile (AIBN)-Au/CeO₂ + Ti-MCM-41-silylated catalytic system results in alkene conversions close to 9% with epoxide decomposition around 90% when working with cumene as an atoning hydrocarbon [161]. The synthesis of meso-structured CeO₂ was performed. Deposition of the Au particles on CeO₂ support was carried out by a deposition-precipitation method with HAuCl₄.3H₂O as the source of Au, following the experimental procedure detailed in [162]. Thus, a solution of 0.2 M of NaOH was added (drop by drop) to 0.6 g of HAuCl₄.3H₂O mixed with distilled water up to 70ml in volume so that the pH of the solution will be regulated to about 10, then poured into 5.7g CeO₂ salt dissolved in distilled water, while stirring so fast. The mixture obtained was continuously stirred at room temperature for 15 to 16 h. Once the solid had been recovered by filtration, it was washed thoroughly with water and oven dried at 100°C for approximately 12 h. Both the solid chemical analysis with X-ray fluorescence (XRF) has it that the Au catalyst on ceria support processed, have a gram % of almost 2.5. Mesoporous TiO₂ was prepared in gram percentage of about 2.1 [163, 164], first of all by mixing 3.11g cetyltrimethyl ammonium bromide in 20.88 distilled water measured in grams. This is accompanied by addition of 5.39 g of tetramethyl ammonium hydroxide together with 0.21g of Ti tetraethoxide to the solution mixture followed by agitation of the solution to ensure complete dissolution of Ti. A gel was obtained on inclusion of 3.43g silica which undergoes agitation in an hour under controlled room temperature. The whole medium is then autoclaved, heated at 100°C for two days under internal pressure. After which the solution is filtered and solid materials were acquired which is washed and dried for a day under a specific temperature of about 60°C. The solid material obtained is air dried under nitrogen flow at 540°C and then further dried under dry air flow also at 540°C in a tubular reactor made of quartz; this is accompanied by room temperature cooling. Ultimately, about 2.1 weight percentage (wt%) catalyst was achieved (expressed as TiO₂) based on chemical analysis. This solid has a specific surface of 1090 m².g⁻¹ with an average pore size distribution of 35 to 38 Å, and has a band in the ultra violet-visible (UV-Vis) spectrum centered at 220 nm. Another catalyst (Ti-MCM-41) was made by first of all drying Ti-MCM-41 at 2.0g in 2 hours under a condition of

temperature (100°C) and pressure (10⁻³) and then allowing it to cool under controlled temperature (room temp) and then 1.88g hexamethyldisilazane solution mixed with 30g of toluene is put on, whole mixture of the solution is then refluxed for 1hour 30min at temperature of 120°C and washed with toluene. This is followed by drying of the catalyst obtained under temperature condition of 60°C. The catalyst is obtained in solid form and weighted two wt% (expressed as TiO₂) based on chemical analysis. This solid has a specific surface of 965 m². g⁻¹, and has a band in the UV-Vis spectrum centered at 220 nm. For comparison purposes samples of the Au/MCM-41 and Au/Ti-MCM-41 have also been prepared. The preparation of a purely siliceous MCM-41 mesoporous material (Si/Al molar ratio =1) was carried out as follows. Typically, 5.0 g of C₁₆TABr was diluted in 33.5 g of water under temperature condition of 40°C. Solution of 8.65g TMAOH measured in percentage weight of about 25 was spread side by side an aerosol weighing almost 1g. And under room temperature condition, mixing together of the final suspension and the early solution of C₁₆TABr obtained was done. Consequently, 4.52 g of the aerosol contained in the resultant solution was hydrolyzed under stirring (350 rpm) at room temperature. The formed gel was maintained under stirring for 1h until complete homogenization. Then, the gel (pH 13.8) was disposed into an internally Teflon-covered autoclave and heated under autogeneous pressure at 135°C for 24h. The obtained solid was filtered off, washed with abundant water, and oven dried at 60°C for 12 h. At last, heating at very high temperature was done in a tubular reactor in order to get rid of the organic substances in the solid, but with further increase in temperature from room temperature to 540 °C (under dry N₂ flow) followed by a step at 540 °C for 6 h (under dry air flow). The Si-MCM-41 sample obtained presents a specific surface area of 1000 m².g⁻¹, with an average pore size distribution of 35 to 38 Å. DP approach was applied in the displacement of the particles of Au on both of the mesoporous materials (silicon/titanium MCM-41) surface. 1.2g HAuCl₄.3H₂O was consistently diluted in 100 ml of water (Milli-Q Quality) and the pH of the obtained solution was modified with drop to drop addition of 0.2 M of NaOH solution until pH 7 to 8 was reached. Then, the mentioned Au-containing solution was added to a suspension of MCM-41 material type measured in 6.0g in a moderate volume of water about 200 ml, followed by strong agitation under controlled room temperature condition. The mixture was maintained under stirring at room temperature for 15 to 16 h. It took one day of drying under temperature condition of about 100°C to achieve the final solid through filtration and prolonged distilled

washing. The Au loading on the MCM-41-type supports was 4.5 and 2.3 wt% for Au/MCM-41 and Au/Ti-MCM41 catalytic samples, respectively, based on XRF measurements [161]. One-pot epoxidation of alkenes can be achieved with hydrocarbons and O₂ having tertiary hydrogen, provided that the proper catalyst combination and one initiator able to form organo Au species, which promotes the formation of the hydrocarbon hydro peroxides, are also present. It is possible to processed organic Au species on Au catalyst support over ceria by photolysis study but the processing of species based on Au peroxide can be derived from infra-ray (IR) studies through interaction of O₂ and Au nanoparticles supported on CeO₂ nanoparticles in the presence of AIBN promoter. These Au-peroxo species are responsible for oxygen to oxygen (O–O) transfer toward the hydrocarbon molecule adsorbed on the solid surface to produce the corresponding organic hydro peroxide which, after desorption, is used for alkene epoxidation. It is possible to achieve a rise in selectivity close to 100% during conversion of alkene in aerobic epoxidation of 1-octene more than it was achieved with two silylated order (Ti and Au catalyst with ceria support). The process, conveniently optimized, can be of interest for improving the efficiency of existing process for the synthesis of PO and which uses organic peroxides as oxidants, and more specifically cumene peroxide [165].

2.2.2.1 Reaction path way of Propylene Epoxidation Au/CeO₂

Although only very few reports (previous or current) directly related to propylene epoxidation of Au/CeO₂ are available, some of the work demonstrated by few researchers most of which are based on theoretical simulations includes; the report of Chen Shilong et al on the reaction pathways of low-temperature CO oxidation on Au/CeO₂ catalyst. Through a comprehensive time-resolved Operando-DRIFTS study of the evolutions of various surface species on Au/CeO₂ catalysts with Au particle sizes ranging from 1.7±0.6 to 3.7±0.9 nm during CO oxidation at room temperature, they showed the size-dependent reaction pathways and their contributions to the catalytic activity. According to this report, the types and concentrations of chemisorbed CO (a), carbonate, bicarbonate and formate species formed upon CO adsorption, their intrinsic oxidation reactivity toward O₂ and roles in CO oxidation vary with the size of supported Au particles. They explained that the intrinsic oxidation reactivity of CO (a) does not depend much on the Au particle size whereas the intrinsic oxidation reactivity of carbonate, bicarbonate and formate species strongly

depend on the Au particle size and are facilitated over Au/CeO₂ catalysts with large Au particles. Their work greatly advances the fundamental understanding of the effect of size of Au/CeO₂ catalysts for low-temperature CO oxidation and creates a way for further studies on the subject matter [166].

2.2.3 Propylene Epoxidation Au/SiO₂

Large number of environmental and industrial reactions requires the use of Au catalyst mostly with support making this catalyst a subject of discussion in research. This advancement is chiefly aligning with oxidation of propene to its oxide which was done in vapor phase in company of Au catalyst on H₂ and O₂ molecule, the central issue at hand is on how to employ distinct ways of making catalyst with appropriate support. The focal point here are; what significance does the catalyst preparation have?, what vital role does pretreatment method play?, what attributes does the support material acquire?, the size of the Au particle along with the amount of load are the center of attention. Possibilities to improve the catalyst productivity by employing promoters and by silylation are also discussed [167].

2.2.3.1 Preparation of Catalysts

Preparation of Meso-porous Ti-MCM-41 and Ti-MCM-48 supports was reported by hydrothermal crystallization process [168]. A modified sol-gel method was utilized to produce three-dimensional sponge-like mesoporous titanasilicates (designated, TiO-SiO) [169]. Ti grafting on TiMCM-41 support was done related to the reported procedures [170]. Extremely well arrayed Ti-containing mesoporous hybrid silsesquioxane were produced [171]. Impregnation approach was employed to process Ti support on non-porous silica [172]. Using DP approach Nano Au particles are deposited on its support [173, 174], employing aqueous solution of H₂AuCl₄ with neutral NaOH as precipitant accompanied by air heating under temperature of 573 kelvin.

2.2.3.2 Effect of Preparation Method and Pretreatment

Deposition-precipitation (DP) approach of synthesizing Au catalyst on Ti formed propene oxide with a maximum selectivity (100%) and a very good conversion (1%) rate under a good temperature condition of about 323 kelvin in company of H₂/O₂, this was a great breakthrough in the last 2-3 decades [173,175]. Catalysts that are not processed

via DP approach are likely not to yield propene oxide. A point to note here is, only catalyst made through the above method can achieve propene oxide (figure 10). This method can deposit hemispherical Au nanoparticles only on the Ti sites of Ti-incorporated SiO₂. A single product of CO₂ is achieved when Au catalyst on double support (Ti-oxide/silicate) is made via impregnation [176]. The difference in product selectivity can be related to the state of dispersion and the connection structure of Au particles on model TiO₂ support surface [177]. DP method deposits Au particles of about 2–5 nm in size on the support in a hemispherical shape, which are attached to the support at their flat planes; usually at plane {111} (Figure 2) [177]. The effect of the contact structure is that the interface area of the particles of Au will be enclosed by large interval. On the contrary, small perimeter interface will be achieved when particles of Au > 50 nm in diameter are stacked on support via impregnation. Maximum reactivity, reasonable efficiency of hydrogen was exhibited by Au catalyst on Ti/Si which was made through operation of a precipitant specifically sodium hydroxide (NaOH) [178], Urea, sodium hydrogen carbonate (NaHCO₃), sodium carbonate (Na₂CO₃) and ammonia (NH₃). During DP of Au on titanasilicates it was observed that catalytic activity decreased with increasing severity of washing [179,180], which might be probably caused by poor interactivity of Au and support resulting to moving away of Au from the surface of support. Partially charged Au nanoparticles are held on the support surface mostly due to electrostatic interaction with charged Ti sites while neutral silica surface cannot react with nanoparticles of Au [179]. The catalyst prepared from unwashed supported precipitate is found to have uniform sized and well-dispersed Au nanoparticles on the support (from TEM observation) showing the best activity [178]. Catalyst calcinations at around 573 K followed by pretreatment in dilute H₂ stream and then dilute O₂ streams at 523 K is necessary to obtain best catalysts performance [181, 169].

Propene epoxidation is a typical example for the novel catalysis of Au nanoparticles deposited on metal oxides.

2.2.3.3 Reaction pathway of propylene epoxidation Au/SiO₂

He Jieli et al report on the reaction pathway for the epoxidation of propylene by oxygen over CuOx/SiO₂ catalysts with and without Cs⁺ modification. In their work, they report that 5 wt% CuOx/SiO₂ catalysts was modified, which catalyst the formation of acrolein.

The kinetic studies explained that the acrolein and PO were formed in parallel as primary products via allylic

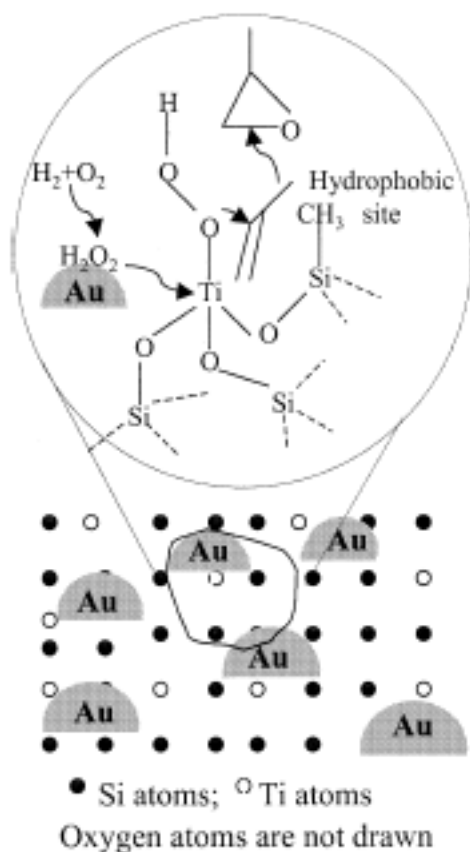


Figure 11: Influence of Au particle size on product yield during propene epoxidation using O_2 and H_2 .

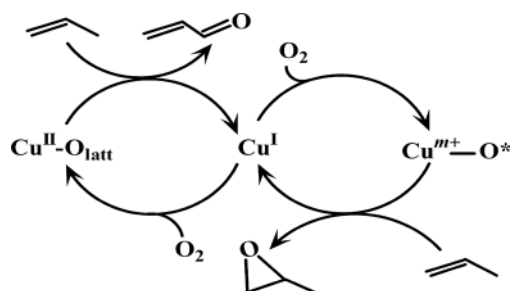


Figure 12: Proposed reaction mechanism for the formations of primary products over the CuO_x/SiO_2 catalysts with and without Cs modification. Cu generated over the CuO_x/SiO_2 catalyst with and without Cs modification during the reaction accounts for the formation of propylene oxide, while the lattice oxygen is responsible for acrolein formation. [182]

oxidation and epoxidation routes over the catalysts with and without Cs^+ modification. The PO undergoes isomerization into allyl alcohol and further oxidation into acrolein over the 5 wt% CuO_x/SiO_2 catalyst without Cs^+ modification. The modification by Cs^+ inhibited the consecutive conversion of PO by decreasing the acidity.

It was observed through pulse-reaction studies that the lattice oxygen species was responsible for the allylic oxidation of C_3H_6 to acrolein. Their report also showed that the lower reactivity of the lattice oxygen of the Cs^+ modified catalyst additionally contributed to the increase in PO selectivity. They proposed that Cu activated O_2 , thereby forming the active oxygen species for the conversion of C_3H_6 to PO. However, if the concentration of Cu sites is very high, this will not favor the selectivity of PO. The fig below is the proposed reaction mechanism for the formation of primary products over CuO_x/SiO_2 catalysts with and without Cs^+ modification. [182]

2.3 Methanol Synthesis

Since the start of the last century, methanol (CH_3OH) synthesis has attracted great interest because of its importance in chemical industries and its potential as an environmentally friendly energy carrier. The catalyst for the CH_3OH synthesis has been a key area of research in order to optimize the reaction process. Several research on CH_3OH synthesis by Cu have been reported because copper still remains the most active catalyst component even though the nature of the active site is yet to be fully understood. Recently, CH_3OH synthesis by various catalyst supports on metal oxide has been studied. This report gives an account of CH_3OH synthesis by Au catalyst support on different metal oxide such as Ti , Si and Ce .

2.3.1 Methanol Synthesis by $Au/ZnO-TiO_2$

This study reports a synthesis of CH_3OH by $Au/ZnO-TiO_2$, Au which was deposited on some oxides with much dispersion was observed active when employed in CO_2 hydrogenation ranging from 150-400°C temperatures. Characteristic features of support oxide determine the selectivity of the product. Elevated CO_2 conversion rate with very low CH_3OH rate is achieved with oxides that are acidic in nature for instance TiO_2 . Importantly, large particle size outcome of Au was observed and smaller Au particles gave higher CH_3OH productivity per exposed surface area of Au , which is because the particles of Au experience decrease in size due to increase in perimeter. Moreover, CH_3OH was acquired from Au support on Zn/Ti because the interface of Au/Zn becomes greater [183].

The combination of ZnO and TiO_2 as oxide component was examined in more detail, because these catalysts gives CH_3OH stability and selectively. From below fig. 12c it can be observed that the amount of zinc in oxide phase

strongly determines the diameter of Au as well as the surface area of BET. The higher the zinc content, the lower the surface area of BET. There will be rise in the surface area of BET if magnesium citrate is introduced however, the presence of Ti in the content of the oxide will result to rise in the diameter of Au gotten from XRD studies. From the outcome of this work it is expressed that the nature of support oxide so much determines how active CH_3OH can be in contrast to Au catalyst on a support, which can be explained as due to the interface site of both Au with its support which is very significant in the processing of CH_3OH [184]. Production of CH_3OH on the basis of selectivity significantly depends on the mixing together of the oxides of Au/Zn, but ZnO function is not well defined. A valuable means of creating Au particles of low size while enlarging the sites of its interface is via combining parts of the TiO_2 in conjunction with magnesium citrate [185].

2.3.1.1 Impact of Oxides Electronegativity

Activity of CO_2 is influenced by acidity of surface Fig. 13 expressed how the electronegativity of the oxides is related to CO_2 conversion at 250°C . The average size of Au particle in catalyst is insignificant, in relation with 5 nm except if the size of the Au is more than 5 for instance 10.5 nm size for Au catalysts on ceria support. The relatively acidic support, TiO_2 , revealed the highest CO_2 conversion with basic support, ZnO, the least. But small activity surface which is likely because CO_2 is activated and adsorbed firmly onto the basic support. Maximum selectivity of CH_3OH is favored by zinc support having the largest basicity

2.3.1.2 Product Selectivity

Fig.14a shows how the products are distributed over some typical Au catalysts. As described before, Au/ TiO_2 gave the highest CO_2 conversion, mostly at low temperatures. CO was the major product at this temperature range, which was obtained by reverse water gas shift reaction, and the yields obtained were very close to equilibrium. At temperatures above 350°C , a large amount of CH_4 was formed over Au/ TiO_2 with selectivity exceeding 50%. Selectivity of Au catalyst support by Al_2O_3 is comparable with Ti support, on the contrary, its CO_2 conversion rate is small at certain temperature (150°C) when compared with using Ti support. Over Au/ZnO and Au/ Fe_2O_3 , CH_3OH was formed with relatively high selectivity in less than 30 atom% and supported on mixed oxides.

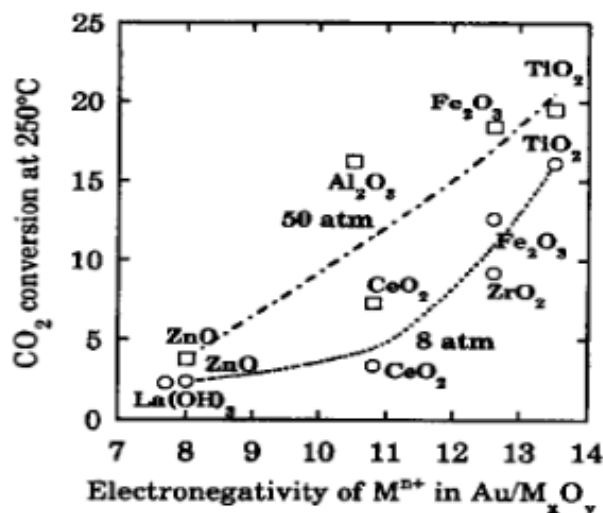


Figure 13: Impact of support oxides acidity in hydrogenation of CO_2

2.3.1.3 Combination of Oxides

The relationship relating CH_3OH production and selectivity at 250°C with reference to several Au catalysts having a metal loading with 33 atom% is shown in fig 12b. CH_3OH whose selectivity is high was observed over ZnO which has Au catalysts. Oxides like Fe_2O_3 and TiO_2 are added to Au/ZnO, chemicals gotten from CH_3OH are enhanced, maintaining high selectivity exceeding that for commercial Cu/ZnO- Al_2O_3 catalyst. Although the Au/ZnO- Fe_2O_3 catalyst confirmed the most elevated CH_3OH yield and selectivity, the stability of the CH_3OH yield at the reaction changed, depending on the pre-reduction conditions.

2.3.2 Methanol Synthesis by Au/ CeO_2

There is only little report on CH_3OH synthesis by Au/ CeO_2 . E.A Shaw et al in their report examine the CH_3OH synthesis activity of Au/ CeO_2 catalysts derived by the oxidative activation of CeAu_2 [186]. Boucher et al also gave a report on CH_3OH synthesis over Au supported on ZnO and CeO_2 Nano shapes. They investigate the active nature of Au clusters supported on ZnO and CeO_2 Nano shapes produced by hydrothermal synthesis for the decomposition, oxidation, and steam reforming of CH_3OH in their report, were Au atoms and clusters (<1 nm) were dispersed on the {110} facets of CeO_2 Nano rods, but only Au nanoparticles (~3 nm) were found on the {100} surfaces of CeO_2 nanotubes. [187]

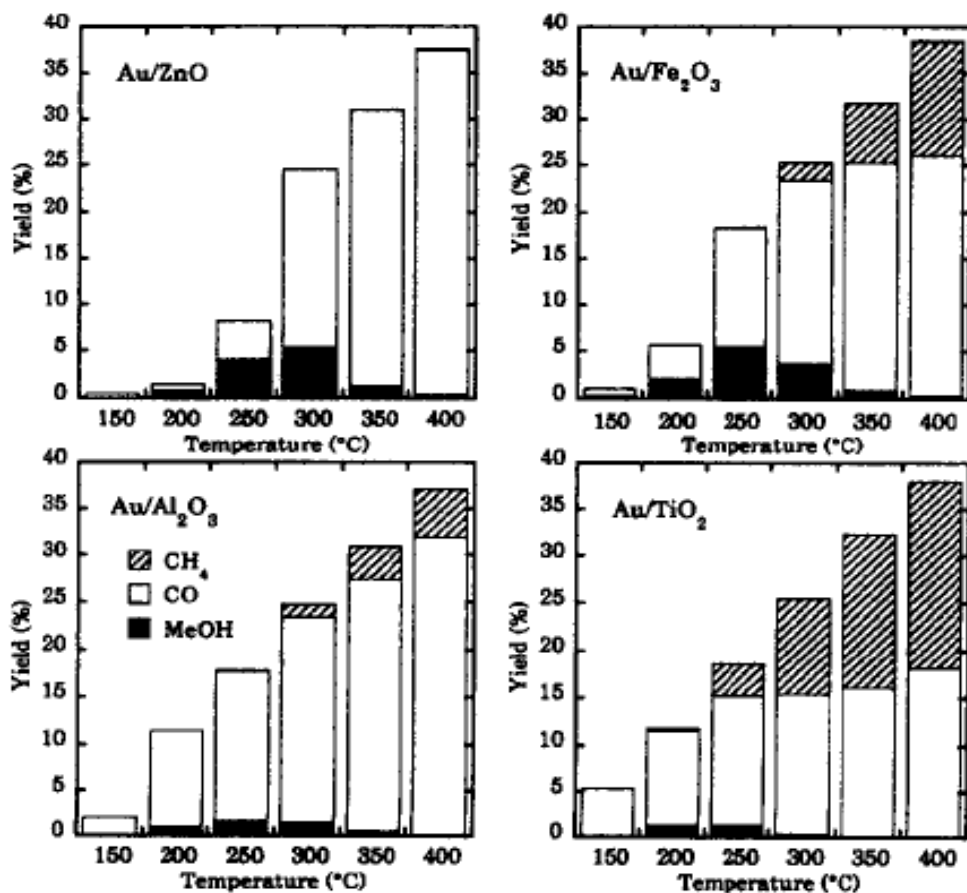


Figure 14a: Distribution of Product in hydrogenation of CO₂ on Au catalyst with support

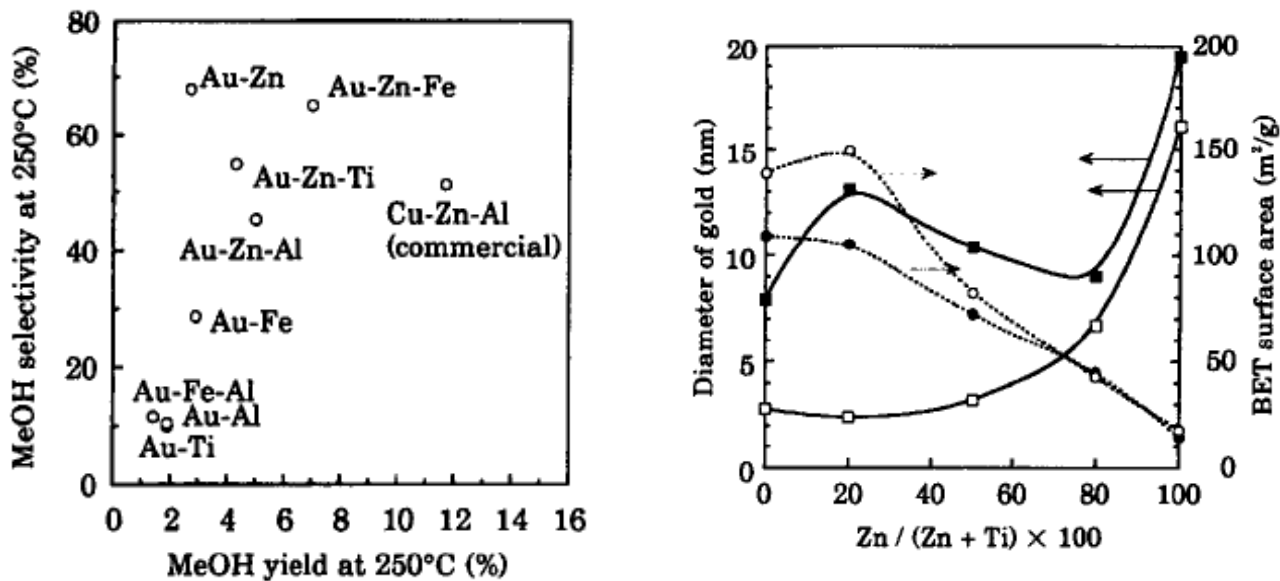
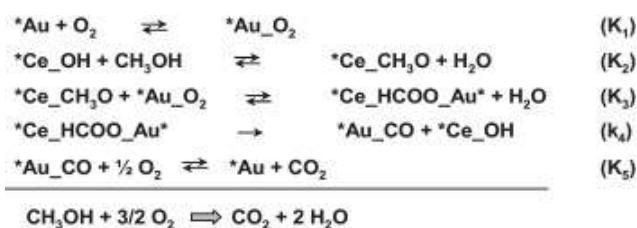


Figure 14b: correlation between CH₃OH yield and selectivity over Au/MO_x/MO_y (Au:M:M1=1:1:1 in atomic ratio)

Figure 14c: Zn content in Au/ZnO-TiO₂ as a determinant factor of surface area of BET and Au diameter. Prepared with Mg-citrate addition/prepared without Mg-citrate addition

2.3.2.1 Mechanism of methanol synthesis over Au/CeO₂

This is according to the work of Basin P et al, who proposed a kinetic model providing the order, kinetic constants and the activation energy for the methanol oxidation mechanism over Au/CeO₂ catalyst through complementary kinetic and FTIR (Fourier transform infrared spectroscopy) **operando** SSITKA (steady-state isotopic transient kinetic analysis) approaches. They studied Au-supporting oxide with high catalytic activity at room temperature towards combustion of methanol as a model VOC (volatile organic compound); they employed complementary kinetic and FTIR **operando** SSITKA approaches which give them access to investigate the mechanism of the reaction. According to the kinetic model which they proposed for the reaction, they discovered that; methanol adsorbs via dissociation on the surface of Ce forming methoxys, linearly and bridged adsorbed methoxys act as an intermediates, transforming then into formates (only in presence of Au in the considered low temperature range), while other types of methoxy species are spectators, formates, whose transformation was found (considering their thermal behavior) to be the rate determining step (RDS) for the reaction, decompose into CO and OH species, this decomposition only takes place in the area of the Au NPs (in a zone identified as an “active perimeter”), where Au oxidizes adsorbed CO to CO₂. The reaction model can thus be represented by the following set of five successive elemental steps.



Where *Au and *Ce are superficial active sites, K_1 , K_2 are adsorption equilibrium constants and K_3 , K_5 are equilibrium constants for steps 3 and 5 respectively.

They assume that the formate decomposition is the rate determining step and hence, the model is then proposed which was further realized through the SSITKA experiment which also gives room for the determination of the activation energy associated to the RDS. The value which they obtained from the SSITKA analysis is some extend less than the apparent activation energy and the difference between the values is consistent with the proposed kinetic model. [188]

2.3.3 Methanol Synthesis by Au/SiO₂

This gives a description of a chemical process making use of Au nanoparticle that serve as a catalyst along with ionic liquids (IL) as solvent for methane (CH₄) oxidation as reported by (T Li et al.). This was how the reaction took place; 100ml autoclave was charged with the following catalyst, solvent, acid reagent, oxidant altogether and accordingly (Au/SiO₂, Cl, trifluoroacetic anhydride/trifluoroacetic acid, K₂S₂O₈). Influence of the catalyst (0.01g)/IL (1g) during CH₄ conversion was reviewed at about 90 degrees temperature while the prime product obtained was CH₃OH. The outcome obtained in % from the above reaction involving both IL and catalysts were as follows; 24.9% obtained during conversion of CH₄, 71.5% obtained as product selectivity with 17.8% yield. % selectivity of CO₂ is 16 with a yield of 0.6%, while H₂ has a selectivity of 0.4% and yields 0.1%. Salvaging of both the catalyst and IL in the reactor will retrieve 96.9 in %. The mechanism associated with the transformation of CH₄ to CH₃OH, including the action of the Nano Au catalyst, was also discussed. [189]

2.3.3.1 Impact of Nano-Au/SiO₂ Catalyst on CH₄ Conversion

Over the years the effectiveness of this catalyst in CH₄ conversion has been tremendous. The outcome reveals that, when no Nano-Au/SiO₂ was found in the reaction system, no conversion of CH₄ could be detected. With an increase in the amount of Nano Au/SiO₂ in the reaction system, the conversion rate, selectivity, and yield increased correspondingly. As the amount of the Nano-Au/SiO₂ reached 0.01g, the conversion rate, selectivity, and yield increased to 24.85%, 71.5%, and 17.8%. Further addition of the Nano-Au/SiO₂ catalyst increased the selectivity limitedly, but lowered the conversion rate and yield rapidly. One possible reason is that, as the level of the Nano-Au/SiO₂ was further increased, side reactions will become more significant and this will accelerate the exchange of the anions of trifluoroacetic acid with the anions of the IL, which will then lead to a decrease in the acidity of the reaction system, thus decreasing the CH₄ conversion rate and yield dramatically. Over the catalyst system of Nano-Au (Au/SiO₂) and IL, the process of CH₄ to CH₃OH was investigated. The significance of the IL as reveal from the effect of this study cannot be overemphasize as it stimulates Au catalyst activity and at the same time enables dissolution, moreover exhibit a reaction with high selectivity. The system of Nano-Au/SiO₂ and IL could be recycled, and conversion of CH₄ in the recycled system

still remained at a high level. There are no environmental implications as regards this technique of oxidation of CH_4 as heavy metals/undiluted Sulfuric acid and other environmentally harmful chemicals were not involved during the reaction. A reaction mechanism was proposed, which indicate that molecular oxygen got consumed in the oxidation–reduction cycle. Consequently, CH_4 oxidation to CH_3OH can be achieved as a green chemical process. The system can also be employed in other green chemical processes of liquid phase or gas phase oxidation.

3 Conclusions and Future Perspective

Remarkably, activities of catalysts having a high degree of support Au catalysts for CO oxidation under room temperature arises from reaction of CO absorbed on the step, the extreme which is the edge, and also the corner of nanoparticles of Au catalyst on oxide support where molecules of oxygen are adsorbed at its circumference area. It is unlikely that oxide Au species and non-metallic small Au clusters are behind the extraordinarily high catalytic activity, although they are active to a certain extent. It is proposed that epoxidation of propylene proceeds by the formation of H_2O_2 on the surfaces of Au particles, capture as OOH at Ti^{4+} in tetrahedral coordination in the matrices of SiO_2 , which include uptake of propylene on the surfaces of the oxide support in the process of OOH reaction. Over the catalyst system of Nano-gold (Au/SiO_2) and IL, the process of CH_4 to CH_3OH was investigated. The significance of IL as revealed from the effect of this study cannot be overemphasized as it stimulates Au catalyst activity and at the same time enables dissolution, moreover exhibit a reaction with high selectivity. The system of Nano-Au/ SiO_2 and IL could be recycled, and conversion of CH_4 in the recycled system still remained at a high level. There are no environmental implications regarding this system of oxidation of CH_4 since heavy metals along with undiluted Sulfuric acid and other environmentally harmful chemicals were not involved during the reaction. A reaction mechanism was proposed, which indicated that molecular oxygen was consumed in the oxidation–reduction cycle. Consequently, CH_4 oxidation to CH_3OH can be achieved as a green chemical process. The system can also be used in other green chemical processes of liquid phase or gas phase oxidation.

CH_3OH is expected to be a potential solution to the partial deployment of fossil source-based economies. Moreover, it is a recognized energy carrier that is better

than other alternatives in terms of transportation, storage and reuse. New or improved catalysts for CH_3OH production are likely to be discovered in the near future. These catalytic materials are expected to allow lowering the temperature and pressure required for the CH_3OH synthesis reaction. With pressure still useful to favor the reaction that is limited by the thermodynamic equilibrium, the current temperature of the CH_3OH synthesis process is over the Huttig temperature, thus promoting the catalyst sintering.

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