Bimetallic Gold-Containing Catalysts for the Selective Oxidation of α-Pinene: The Formation of a Green Natural Monomer

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Abstract

Various bimetallic (i.e., Au-M, where M=Pd, Cu, Co or Fe) gold-containing catalysts were prepared and tested for the oxidation of α-pinene. All catalysts were prepared by impregnation method on TiO₂ support and compared to determine the best and most active catalyst for the selective oxidation of α-pinene. Although, the reaction resulted in the formation of a variety of products including: pinene oxide, verbenol, verbenone, carveol, and carvone, however the emphasis was on studying the effect of increasing the catalytic mass and reaction time, particularly during the conversion of α-pinene to pinene oxide. Other catalysts namely, CoCu, Cu, PdCu, FeCu, Pd and Fe were studied for comparison. After 24 hours, the catalytic activity of all the studied systems was observed to be in the order of: CoCu>Cu>AuCu>PdCu>FeCu>PdAu>Au>Pd>Fe>AuFe. Furthermore, the bimetallic AuFe/TiO₂ system was found to be the best and most active catalyst for the selective conversion of α-pinene to pinene oxide after 24 hours at a temperature of 70 °C. The mass of the catalyst and reaction time greatly influenced the oxidation rate of α-pinene.

Keywords: Bimetallic catalyst; α-pinene; Gold catalyst; Green monomers

Introduction

Softwood such as coniferous trees like pines are important sources of terpenes like α-pinene, which can be used to provide renewable raw materials for the manufacturing of other valuable fine products [1-4]. For instance, α-Pinene is the main constituent of gum turpentine [5-8], which is considered as a renewable and inexpensive starting material for producing various materials such as medicines, fragrances, agrochemicals, and flavors [9]. α-pinene is one of two isomers of pinene, which contains a reactive four-membered ring. The oxidation of α-pinene will be industrially important since it enables transformation of readily available and inexpensive substrates to valuable chemicals through catalytic employed processes.

For polymer scientists, the development of new renewable monomers and polymers from natural resources has increasingly gained attention from scientists. α-Pinene is the most abundant of the terpenic compounds which could serve as an ideal green and sustainable monomeric materials. Unfortunately, the polymerization of α-pinene proceeds with a relatively low yield [10]. However, in recent years researchers reported the successful polymerization of α-pinene oxide via ring opening polymerization. Kheira et al. [11] studied the cationic polymerization of α-pinene oxide with heterogeneous clay catalyst. The poly (α-pinene oxide) was prepared from α-pinene oxide using Magnnite H⁺ as a catalyst. The authors showed that the polymerization proceeded smoothly and a simple filtration step was sufficient to recover the catalyst. The successful polymerization of this monomer could open the door to create new and green polymers with a wide range of mechanical properties that positions them ideally for various applications such as plastic packaging, cosmetic and medical applications [12].

Currently, the challenging goal to polymer scientists and chemists is to develop catalytic methods suitable for the selective oxidation of α-pinene using green oxidants. Various catalytic materials have been reported including both heterogeneous and homogeneous catalysts [1-4], however the use of green and efficient catalysts is still actively investigated. Catalysts based on gold nanoparticles deposited on several solid supports, particularly on reducible oxides such as CeO₂, TiO₂, Fe₂O₃, Fe₃O₄, and ZrO₂ have attracted substantial attention as highly eco-friendly, and active catalysts utilized in hydrogenation, oxidation and hydrochlorination reactions [1]. Also, bimetallic catalysts now exist with an advantage of catalytic activities that transcend those of their monometallic analogues [1]. In recent years, bimetallic gold-containing catalysts have drowned a considerable attention particularly for the oxidation of α-pinene. For instance, a series of bimetallic catalysts...
Au-M (M represents transition metals such as Co, Cu and Ru) were efficiently supported on TiO$_2$ through deposition-precipitation method and utilised to oxidise α-pinene with a remarkable activity. It was found that the alloyed particles were capable of converting α-pinene concordant as follows: AuCu/TiO$_2$ being the most active, followed by AuCo/TiO$_2$, then Cu/TiO$_2$, followed by Au/TiO$_2$, and lastly AuRu/TiO$_2$ as the least active [13]. By comparison, Au-Cu/TiO$_2$ was observed to be the most selective and active catalyst towards the formation of verbenone [13].

In most heterogeneous catalysts, the lack of stability is a challenging goal to organic chemists. For instance, during oxidation of α-pinene, agglomeration of particles often blocks the active site of the catalyst, contributing to its instability. As mentioned above, TiO$_2$ has been developed and used as a successful alternative support for heterogeneous catalyst [14-17]. TiO$_2$ has high surface area that stabilises the catalysts, especially in its mesoporous structure. Also, TiO$_2$ as a support on heterogeneous catalysts influence bifunctional mechanism. It enforces an electronic effect, which allows for the promotion of the electrocatalytic characteristics of hyper-d-electronic noble catalyst surface atom by the hypo-d-electronic Ti3+ [14]. In addition, it has high activity for several oxidation and reduction reactions at low temperatures and pressures. Moreover, TiO$_2$ is a superior metal oxide catalyst support owing to its chemical stability, strong metal support interaction, and acid-base properties. These properties provide high potential applications for the heterogeneous TiO$_2$ supported catalysts in the synthesis of fine chemicals and photocatalyst-related applications [14].

Impregnation is the simplest known method used for the preparation of gold-supported catalysts. It comprises of wetting the support using an aqueous solution consisting of the metal precursor, normally AuCl$_3$ or tetrachlorauric acid (HAuCl$_4$) [18-22]. Subsequently, the sample is dried, and a thermal treatment then conducted to reduce the precursor into metallic particles [18]. The thermal treatment could be conducted under an oxidizing gas such as oxygen or reducing gas such as hydrogen; in both cases, Au is reduced due to the instability of Au (III) compounds. The limitation of impregnation method is that the Au precursor’s chlorides are also present on the support, leading to the formation of large gold particles [18]. However, despite the drawback, this method can be employed with wide variety of supports [18].

The present study aims at testing the selective oxidation of α-pinene to pinene oxide with different catalysts using TiO$_2$ as a support that has been prepared by an impregnation method. This could open the door for the large-scale production of new renewable materials which can be used as ideal green and sustainable monomers from abundant natural resources.

**Experimental**

**Materials**

TiO$_2$ was used as a catalyst support and HAuCl$_4$•H$_2$O was used as the gold source. Metals which included Cu, Fe, Pd, Co were used as a chloride or nitrate salt. α-pinene (98%) was used as received.

**Catalysts preparation by impregnation method**

The catalysts prepared included 5% Au/TiO$_2$, 5% Cu/TiO$_2$, 5% Pd/TiO$_2$, 5% Re/TiO$_2$, 2.5wt% Co+2.5%wt Cu/TiO$_2$, 2.5wt% Au+2.5wt% Cu/TiO$_2$, 2.5wt% Pd+2.5wt% Cu/TiO$_2$, 2.5wt% Fe+2.5wt% Cu/TiO$_2$, 2.5wt% Pd+2.5wt% Au/TiO$_2$, 2.5wt% Au+2.5wt% Fe/TiO$_2$.

The impregnation method for preparing the supported metal catalysts was conducted in accordance to the description given in references [23-26]. In its essential features, the impregnation method required that the support be contacted with a specific quantity of solution of the metal precursor, normally a salt, and then aged, dried and calcined. Wet” or “soaking” impregnation involved the utilization of the excess amount of the solution with respect to the support’s pore volume. The system was left to age for a specific amount of time under stirring, then filtered and dried.

In a typical experiment, 0.067g of copper (II) chloride was weighed into a beaker. Then, 2.5ml of HAuCl$_4$ added to the beaker that contained copper (II) chloride. The solution was then stirred until the copper salt dissolved into the Au solution. After which 0.95g of TiO$_2$ was added to the AuCu solution and stirred until an even mixture was formed. The drying process was then conducted as follows: 10mg of an aqueous solution of HAuCl$_4$+3H$_2$O was added to 0.95g of the support under stirring. The paste formed was then dried at 110 °C for 16 hours and calcined in static air, typically at 400 °C for 3 hours, to reduce the precursor into metallic particles.

**Reaction setup**

The oxidation of α-pinene was conducted in accordance with the description provided in references [1,3]. In a typical experiment, the oxidation of α-pinene was carried out in a multiple reactors with a magnetic stirrer (1000rpm), maintained at 70 °C and P(O$_2$)=2bar. During the reaction, 2g (2.33ml) of α-pinene (98%), and 20mg of catalyst was constantly stirred in order to obtain the homogenous combination of catalyst with the reaction mixture. Next, the reaction progress was monitored by taking samples at different time intervals (4 and 24h). Analysis of the products was carried out using Gas Chromatography-Flame Ionization Detector (GC/FID).

**Results and Discussion**

**Conversion of α-Pinene to its oxidized products**

Oxidation of α-pinene proceeded smoothly at 70 °C over all the Au-M/TiO$_2$ catalysts prepared by the impregnation method. According to GC/FID results, the observed oxidation products were mainly pinene oxide, verbenol, verbenone, carveol, and carvone. This is in line with the observations from various studies in the literature [27-29]. For instance, Erman [27] reported that catalytic oxidation of α-pinene can yield α-pinene oxide. Silva et al. [28] finding also supports the observation of the present study. Others also reported that cobalt catalyzed α-pinene oxidation can yield α-pinene oxide, carveol, verbenone, and verbenol. Similarly, Pruinier [29] back up the observation of the present study by stating that carvone is one of the products resulting from oxidation of α-pinene.
In our study, the response factors obtained were utilized when calculating selectivity and conversion of α-pinene as well as its oxidation products as presented in Table 1 and Figure 1. From Table 1 and Figure 1, the conversion of α-pinene to its oxidized products under 5% Fe/TiO₂ catalyst prepared by impregnation method was only 5.8% at a temperature of 70 °C and a time=4h. This conversion was highly selective to the formation of carvone (8.7%), then verbenol (7.1%), followed by verbenone (6.7%), and lastly carveol (2.9%).

Table 1: Oxidation of α-pinene with 20mg of 5% Fe/TiO₂ at time=4h; temperature=70 °C; P(O₂)=2bar and 1000r.p.m. stirrer speed.

|                | Area     | Response Factor | Moles   | Conversion % | Selectivity % |
|----------------|----------|-----------------|---------|--------------|---------------|
| Pinene         | 6.39E+08 | 1.20E+11        | 0.0052597 | 5.8          |               |
| Pinene Oxide   | 17259542 | 1.10E+11        | 1.50E-04 | 47.2         |               |
| Vebenol        | 2475239  | 1.10E+11        | 2.33E-05 | 7.1          |               |
| Carveol        | 2459243  | 1.10E+11        | 2.19E-05 | 6.7          |               |
| Vebenon        | 1028992  | 1.10E+11        | 9.30E-06 | 2.9          |               |
| Carvone        | 3178787  | 1.10E+11        | 2.83E-05 | 8.7          |               |
| Unknown        | 9877083  | 1.10E+11        | 8.93E-05 | 27.4         |               |
| Total Product  |          |                 | 3.30E-04 |              |               |
| Total          |          |                 | 0.0055856|              |               |

Figure 1: Oxidation of α-pinene with 20mg of 5% Fe/TiO₂ at time=4h; temperature=70 °C; P(O₂)=2bar; and 1000rpm stirrer speed.
Figure 2: Conversion of α-pinene by 20mg of different catalysts at time=4h; temperature=70 °C; P(O₂)=2 bar and stirrer speed of 1000 r.p.m.

Figure 2 indicates that the order of conversion of α-pinene to its oxidized products was CoCu>PdCu> AuCu>Pd>FeCu>Co>Fe. CoCu/TiO₂ catalyst showed the highest conversion because its particles were finely distributed on the support. Just as found by Ajaikumar et al. [1], of all the prepared catalysts they tested, AuCu/TiO₂ showed the highest catalytic activity in the conversion of α-pinene followed by AuCo/TiO₂. Therefore, it is that CoCu/TiO₂ show the highest conversion as reflected on the results shown in Figure 2.

Selectivity study of the oxidation of α-Pinene

From Figure 3, one can see that the monometallic Au/TiO₂ supported catalyst prepared by impregnation method was highly selective in the formation of pinene oxide (51.50%) at a temperature of 70 °C and time=4h. However, Fe/TiO₂ catalyst prepared by impregnation method was highly selective in the formation of verbenol (7.14%) and carvone (8.68%) and a temperature of 70 °C and time=4h. Under the same conditions, the bimetallic AuCu/TiO₂ catalyst prepared by impregnation method was highly selective in the formation of verbenone (7.18%). Also, CoCu/TiO₂ prepared by the same method used to prepare the previously mentioned catalyst was highly selective in the formation of carveol (18.76%) at 70 °C and time=4h.

Ajaikumar et al. [1] also found that the bimetallic AuCu titania supported catalyst prepared by deposition precipitation method is highly selective towards the formation of verbenone. On the contrary, they observed that AuRu/TiO₂ prepared with the same method they used to prepare AuCu/TiO₂ was highly selective towards the formation of verbenol (22.1%) at 70 °C [1]. It is clear that their result achieved a higher percentage of verbenol selectivity as compared to that of the present study. Perhaps this was so because of the differences in reaction time and conditions.

In our study, an interesting feature also occurred after 4 hours when Au/TiO₂ prepared by impregnation method was observed to be the most suitable catalyst in the conversion of α-pinene to the compound of interest, pinene oxide. On the contrary, Ajaikumar et al. [1] noticed that the monometallic Au titania supported catalyst prepared by deposition precipitation method yields lower conversion than its bimetallic systems, and that it shows high activity towards the production of t-butyl pinene peroxide. The catalytic activity of Fe/TiO₂ also requires further study, as the catalyst showed high activity in the selective formation of verbenol and carvone within 4 hours.

Figure 4 shows that the bimetallic 2.5wt% Fe+2.5wt% Au/TiO₂ catalyst prepared by impregnation method achieved the best selectivity of pinene oxide (51.69%), and so this catalyst proved to be the best among all the tested catalysts in the selective oxidation of α-pinene to form pinene oxide. Unfortunately, the oxidation of α-pinene to form pinene oxide over gold supported catalysts has been limitedly studied. Much of the attentions have only been focused on the conversion of α-pinene to common products like verbenone. Nonetheless, Karlsson [30] studied the oxidation of α-pinene to form pinene oxide under different catalysts for 22 hours. In Karlsson [30] study, Nb/SiO₂ showed the highest catalytic activity of only 10.1% in the selective conversion of α-pinene to pinene oxide. Therefore, the yield from the present study indicates that FeAu/TiO₂ catalysis is the best in the selective conversion of α-pinene to pinene oxide.
Figure 4: Products selectivity by 20mg of different catalysts at time=24h; temperature=70 °C; P(O2)=2 bar and stirrer speed of 1000 r.p.m.

**Table 2:** Conversion of 2 grams of α-pinene over 10mg, 20mg and 50mg of 2.5wt%Pd+2.5wt%Au/TiO2 at time=24h; temperature=70 °C; P(O2)=2 bar, and stirrer speed of 1000r.p.m.

| Catalyst                | Mass/mg | Conversion % | Selectivity % |
|-------------------------|---------|--------------|---------------|
| 2.5wt%Pd-2.5wt%Au/TiO2 | 10      | 35.89        | 49.43         |
| 2.5wt%Pd-2.5wt%Au/TiO2 | 20      | 44.17        | 35.25         |
| 2.5wt%Pd-2.5wt%Au/TiO2 | 50      | 48.91        | 26.56         |

**Effect of catalyst mass on the oxidation of α-Pinene**

From the results presented in Table 2, it is clear that any increase in the mass of catalyst increases the conversion of α-pinene, but decreases the selectivity of pinene oxide. Balázs et al. [33] previously studied the effect of increasing mass (concentration) of the catalyst on α-pinene conversion. Although their study was slightly different from that of the present study, there is a close link between the two researches. Balázs et al. [33] studied the effect of catalyst concentration on the selective conversion of α-pinene to camphene. Their reaction was conducted at 130 °C, utilizing different α-pinene/catalyst ratios, as follows: 100/0.25, 100/0.5 and 100/1. They observed that the selectivity of camphene reduced when the ratio α-pinene/catalyst was increased, implying that selectivity decreased with an increase in concentration (loading) of the catalyst. Perhaps this is attributed to the weak stability of the camphene, which may eventually lead to the formation of other α-pinene derivatives. Similarly, the concept of Balázs et al. [33] can be used to explain why selectivity of pinene oxide decreased when the mass of the catalyst was increased. Increasing the mass of the catalyst lowers the stability of pinene oxide formed, causing it to form other α-pinene derivatives.

Balázs et al. [33] observed an interesting (but same with the observation from the present study) phenomenon when the mass of the catalyst was increased during conversion of α-pinene to form camphene. These scholars observed that four days were required for a desired conversion of α-pinene when less catalyst (in the ratio of 100/0.25) was utilized, but only a few minutes was enough when more catalyst was added (in the ratio of 100/1). Their observation
is in line with that from the present study since the conversion of α-pinene increased with an increase in the catalytic mass. Indeed, this is because of the fact that any increase in the mass of the catalyst increases the surface area of the catalyst [34].

**Effect of reaction time on the oxidation of α-Pinene**

The results presented in Table 3 indicate that the conversion of α-pinene increases as time increases. Ajakumar et al. [1], Yan Chun [35], Rachwalik et al. [36] also studied the influence of time of reaction on the selective conversion of α-pinene. Interestingly, both of them noticed that the conversion of α-pinene increases with any increase in the reaction time. Ajakumar et al. [1] studied the effect of reaction time on oxidation of α-pinene by carrying out the reaction at various reaction times and varying the temperature from room temperature to 90 °C. They observed that the oxidation of α-pinene selectively increased when the reaction time was increased up to a temperature of 70 °C [1]. However, these scholars also noticed that there was no significant change in the distribution of products as time increased at room temperature [1].

**Conclusion**

The catalytic oxidation of α-pinene over various monometallic and bimetallic gold-containing catalysts prepared by impregnation method was studied at a temperature of 70 °C. The major products formed were pinene oxide, verbenol, verbenone, carveol, and carvone. The monometallic Au/TiO₂ catalyst prepared by impregnation method proved to be the best catalyst for the selective conversion of α-pinene to form the desired product of pinene oxide, after only 4 hours. However, after 24 hours of the reaction time, the bimetallic 2.5wt% Fe+2.5wt% Au/TiO₂ catalyst prepared by impregnation method achieved the best selectivity for the formation of pinene oxide with the greatest percentage yield during the entire reaction, making it the best catalyst for oxidation of α-pinene to form pinene oxide.

Other catalysts apart from the AuFe/TiO₂ system also showed efficient results during the oxidation of α-pinene. For instance, CoCu titania supported catalyst prepared by impregnation method showed the highest conversion of α-pinene with a beneficial percentage yield after 24 hours. The same catalyst was found to be highly selective in the formation of carveol. Generally, the order of conversion was observed as CoCu>Cu>Fe/Pd Cu>PdAu>Fe/Au>Fe after 24 hours.

Similarly, 2.5wt%Pd+2.5wt%Cu/TiO₂ catalyst prepared by impregnation method was found to be highly selective in the formation of verbenol after 24 hours. On the other hand, 5.5wt% Cu/TiO₂ prepared by impregnation method was observed to be the best catalyst in the selective oxidation of α-pinene for 24 hours to yield verbenone.

The effect of increase in mass of the catalyst and reaction time on the conversion of α-pinene was also studied. It was observed that the catalytic conversion of α-pinene increased when the reaction time was increased. Selectivity was also observed to increase when the reaction time was increased. Nonetheless, although an increase in mass of the catalyst led to an increase in conversion of α-pinene, selectivity was greatly reduced.

This study provided useful insight in the application of gold-bimetallic catalysts in the selective oxidation of α-pinene, especially in the production of pinene oxide as the desired product. From the present study’s observations, it can be deduced that the bimetallic AuFe/TiO₂ catalyst prepared by impregnation method is active and selective towards the formation of pinene oxide over the oxidation of α-pinene at a temperature of 70 °C for 24 hours. Considering this observation, it would be economical to produce pinene oxide from α-pinene with a beneficial percentage yield after 24 hours.

**Table 3: Oxidation of α-pinene over 2.5wt%Fe+2.5wt%Au/TiO₂ at varied time; temperature=70 °C; P(O₂)=2 bar; and stirrer speed of 1000r.p.m.**

| Catalyst                  | Mass/mg | Time/h | Conversion % | Pinene oxide % |
|---------------------------|---------|--------|--------------|----------------|
| 2.5wt%Au-2.5-wt%Fe/TiO₂   | 20      | 0.5    | 4.63         | 45.88          |
| 2.5wt%Au-2.5-wt%Fe/TiO₂   | 20      | 1      | 5.2          | 44.3           |
| 2.5wt%Au-2.5-wt%Fe/TiO₂   | 20      | 2      | 5.73         | 45.75          |
| 2.5wt%Au-2.5-wt%Fe/TiO₂   | 20      | 4      | 6.3          | 48.46          |
| 2.5wt%Au-2.5-wt%Fe/TiO₂   | 20      | 6      | 10.41        | 43.72          |
| 2.5wt%Au-2.5-wt%Fe/TiO₂   | 20      | 24     | 23.87        | 51.69          |

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| Verbenol | Verbenone | Carveol | Carvone | Unknown |
|--------|-----------|---------|---------|---------|
| 10.32  | 7.69      | 5.92    | 8.36    | 25.99   |
| 7.71   | 20        | 4.81    | 5.54    | 26.39   |
| 6.91   | 6.52      | 3.15    | 7.67    | 28.25   |

| 4.39  | 2.81      | 13.92   | 4.93    |
| 4.53  | 6.67      | 29.02   | 3.13    |

Selectivity %

Pinene oxide Mass/mg 7.69 48.46 43.72 6.67 20
Time/h 5.63 25.99 Conversion 4 5.82 4.93 4.63 20
Unknown 0.5 Carvone 7.87 4.53 10.32 5.2 10.41 2.81 6.06 8.18 20
20 3.15 Verbenone 28.25 15.65 24.29 4
Carveol 51.69 3.13 24 8.36 44.3 7.2 7.71 29.02 45.75 4.39 1 5.73 5.54 26.39 6.91 20 6.29 6 20 8.77 5.92 26.39 3.15 34 33 32 31 30 29 28 27 26 24 23 22 21 20 19 18 17 16 15 14 13 12 11 8 7 6 5 4 3 2 1

Formation of a Green Natural Monomer

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