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Research Article

Synthesis of Carboxylic Acid by 2-Hexenal Oxidation Using Gold Catalysts Supported on MnO_2

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Synthesis of carboxylic acid can be achieved by the oxidation of aldehyde using air as an oxidant in the presence of a potential catalyst. We demonstrated that 2-hexenal can be oxidized to carboxylic acid by Au, Pd, and Au-Pd catalysts and investigated the effects of catalyst support (graphite, TiO_2, MgO, SiC, MnO_2, CeO_2, and Al_2O_3), preparation method for supported catalyst (sol immobilization, impregnation, and deposition precipitation), and choice of catalyst components. Analysis of conversion% and selectivity% for 2-hexenoic acid showed that MnO_2-supported gold nanoparticles are the best catalysts for 2-hexenal oxidation. Moreover, catalysts prepared by sol immobilization are the most active possibly due to the much smaller gold nanoparticle size. Selectivity for 2-hexenoic acid is a major pathway of oxidation of 2-hexenal.

1. Introduction

Oxidation plays a key role in the synthesis of chemical intermediates for the manufacture of high-value fine chemicals, agrochemicals, pharmaceuticals, and high-tonnage commodity chemicals. The oxidation of aldehyde to carboxylic acid is an important synthetic transformation [1], and it is considered to be a commonly encountered organic chemistry reaction [2]. These oxidation reactions often use stoichiometric oxygen donors such as chromate or permanganate, which results in the production of a large amount of environmental toxins. Therefore, finding environmentally friendly alternatives is crucial, and the ultimate goal is to efficiently use molecular oxygen from air with an oxidation catalyst. Oxidation with molecular oxygen under green oxidation methods has been a very attractive proposition in recent years, and gold catalysts are effective for the oxidation of alcohols [3], oxidation of hydrogen to hydrogen peroxide, and oxidation of alkenes [4–7]. Later, it has been found that the supported gold nanoparticles are efficient catalysts for several oxidation processes. Marsden et al. [8] reported that gold nanoparticles can oxidize an aldehyde, which had been dissolved in a primary alcohol, to ester, while Choudhary and Dumbre [9] showed that MgO-supported nanogold catalyzes the oxidation of aldehyde in the presence of molecular oxygen at temperatures above 120°C. In addition, supported gold has been used as a catalyst for the oxidation of 5-hydroxymethylfurfural (HMF) to 5-hydroxymethyl-2-furandicarboxylic acid (HFCA) [10–13]. Moreover, Davis et al. [14] used supported metal catalysts, such as Pt/C, Pd/C, and Au/C, for oxidation of HMF at a temperature of 22°C and with 690 KPa of oxygen, and they demonstrated that gold supported on carbon had a higher reaction rate and that HFCA was the major product. Pasini et al. investigated the influence of bimetallic gold-copper on HMF oxidation [13] and showed that Au-Cu catalyst supported on TiO_2 was more active than monometallic gold. Biella et al. [15] showed that gold was a highly active catalyst for propanal and butanal oxidation under 300 KPa of oxygen pressure at 363 K in water. More recently, Wan et al. reported that carbon nanotube-supported Au-Pd alloy nanoparticles were highly efficient and recyclable heterogeneous catalysts for the aerobic oxidation of HMF in water under base-free conditions [16].

The present study evaluated whether aldehyde oxidation can be catalyzed by supported gold or gold-palladium nanoparticles to the corresponding carboxylic acid using molecular oxygen from the air. This study also investigated whether 2-hexenal can be oxidized selectively under mild, solvent-free green conditions with high selectivity to the corresponding carboxylic acid. Moreover, the reaction conditions, namely, the support, reaction temperature, catalyst preparation methods, and choice of metal, were optimized.

2. Experimental

2.1. Materials. $PdCl_2$ and $HAuCl_4 \cdot 3H_2O$ were purchased from Johnson Matthey. All other chemicals were purchased from Sigma-Aldrich.

2.2. Catalyst Preparation. Catalysts were prepared by sol immobilization, impregnation, and deposition precipitation methods using standard procedures. For all catalysts, the concentration of metal is expressed as weight percent of the combined metal and solid support material.

2.2.1. Sol Immobilization. Monometallic (Au, Pd) and bimetallic (Au-Pd) catalysts were prepared using sol-immobilization method. The detailed procedure for the preparation of 1% (w/w) Au-Pd/MnO_2 catalyst is explained here for an example. Aqueous solutions of $PdCl_2$ (1.1698 mL from the stock of 6 mg in 1 mL), $HAuCl_4 \cdot 3H_2O$ (1.06003 mL from the stock solution of 12.25 g in 1 L), and polyvinyl alcohol (1% solution, MW = 10000, 80% hydrolysed) were prepared and mixed together by stirring for 15 min. To this solution, freshly prepared 0.1 M of $NaBH_4$ (>96%, $NaBH_4$/Au, mol/mol = 5) was added and stirred for 30 min. After adjusting the pH to 1, by adding sulphuric acid, manganese dioxide (MnO_2, 1.98 g) was added and stirred for 1 h to make a slurry. The slurry was filtered, and the recovered catalyst was washed with 2 L distilled water and dried (110°C, 12 h).

2.2.2. Impregnation. Preparation of 1% (w/w) Au/MnO_2 catalyst was done by impregnation. In short, 0.816 mL of $HAuCl_4 \cdot 3H_2O$ solution (12.25 g in 1 L) was added to MnO_2 (0.99 g) and stirred until it formed a paste. The paste was dried (110°C, 16 h) and calcined in static air (400°C, 3 h).

2.2.3. Deposition Precipitation Using NaOH. Deposition precipitation (DP) method was also used to prepare 1% (w/w) Au/MnO_2 catalyst as follows: MnO_2 solution was first prepared by mixing MnO_2 with distilled water (0.99 g in 150 mL) and stirring at 60°C. 0.816 mL of $HAuCl_4 \cdot 3H_2O$ solution (12.25 g in 1 L) was added and stirred for 1.5 h. The pH was adjusted to 9 by the dropwise addition of NaOH solution (0.1 M). At the end, filtration method was used to recover the catalyst. Then, the catalyst was washed with distilled water (1 L) to remove impurities, dried (110°C, 16 h), and calcined in static air (400°C, 3 h).

2.3. Catalyst Testing and Characterization. 2-Hexenal oxidation was carried out using air in a glass reactor, which consists of a round-bottom flask and a reflux condenser and heating source. In short, the substrate (4.23 g) was mixed with the catalyst (0.06 g) and stirred for 24 h at 50°C. Once the reaction was completed, the reaction mixture was analyzed using gas chromatography (Varian Star CP-3800) with a CP-wax 32 column and a flame ionisation detector.

Table 1: Effect of support on 2-hexenal oxidation.

Catalyst	Conversion%	Selectivity%	
		Dimer	2-Hexenoic acid
Graphite	0.7	0	93.1
Au/G	74.5	4.0	86.0
TiO_2	0.9	0	96.5
Au/TiO_2	68.2	2.9	88.4
MgO	1.1	0	89.3
Au/MgO	54.0	6.2	85.9
SiC	0.7	0	92.1
Au/SiC	69.3	4.1	82.8
MnO_2	0.8	0	95.6
Au/MnO_2	81.3	8.3	89.1
CeO_2	1.2	0	90.5
Au/CeO_2	72.8	4.3	84.6
Al_2O_3	0.4	0	89.0
Au/Al_2O_3	65.4	4.8	84.2

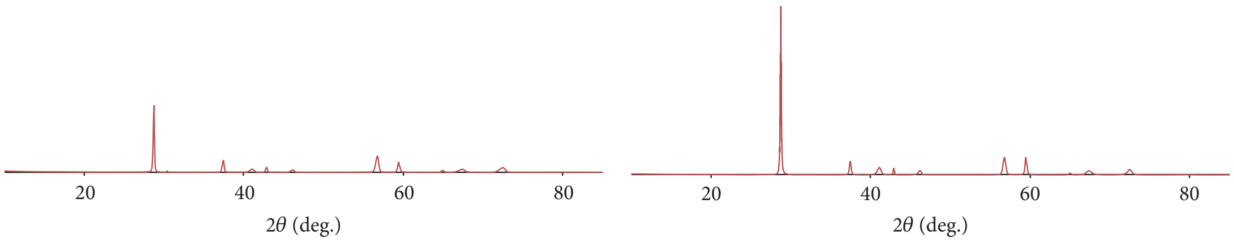
Reaction conditions: 4.23 g of 2-hexenal, 0.06 g of catalyst, 50°C, 24 h, atmospheric pressure.
Dimer: 4,6-dipropyl-3,4,5,6-tetrahydropyran-2-one-5-carboxaldehyde.

2.4. Transmission Electron Microscopy. To prepare the samples, the powder catalyst was dispersed in ethanol, and the suspension was dropped onto a lacey carbon coated 300-mesh copper grid. Sample analysis was carried out by transmission electron microscope (JEOL 2100) equipped with a lanthanum hexaboride filament (200 kV).

2.5. X-Ray Powder Diffraction (XRD). The catalysts were ground into powder and then placed in a sample holder. The XRD analysis was performed using a PANalytical X'Pert Pro with CuK_α X-ray source operated at 40 kV and 40 mA fitted with an X'Celerator detector.

3. Results and Discussion

Activity of catalyst can be affected by several factors, including the nature of the catalyst support. Catalyst supported by different materials showed different activities and selectivity, even under the same conditions [17, 18]. This research work was performed to examine the effect of the support on 2-hexenal oxidation. The reactivity of the pure supports alone in the absence of gold was fairly minimal with 2-hexenoic acid being the major product. The addition of gold supported on graphite or metal oxide, however, leads to a significant increase in the conversion of the 2-hexenal as shown in Table 1. Five different oxides were analyzed for their potential to be a catalyst support in the liquid-phase oxidation of 2-hexenal and compared with graphite and silicon carbide (Table 1). Among the five different supports tested in the study, Au catalyst supported on MnO_2 showed greater activity. These supports can be divided into reducible (TiO_2, CeO_2, and MnO_2) and irreducible (Al_2O_3 and MgO) supports. The latter have a low capacity for adsorbing or storing oxygen [19], which may explain the higher activity that was observed when using reducible supports, relative to



(a)

(b)

FIGURE 1: The XRD pattern of (a) 1% Au/MnO_2 and (b) MnO_2.

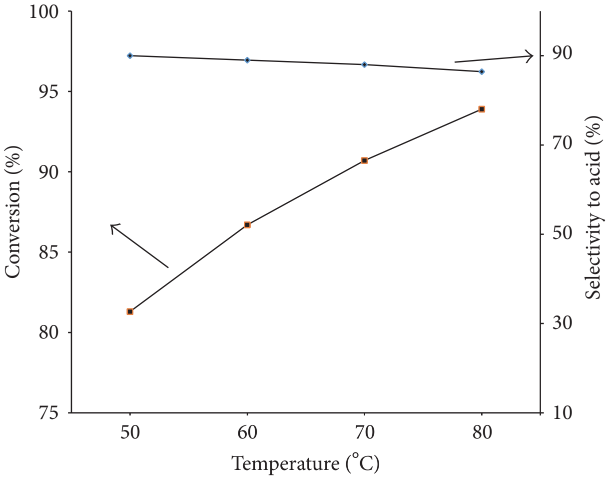


FIGURE 2: Effect of temperature on 2-hexenal oxidation using Au/MnO_2. Reaction conditions: 4.23 g of 2-hexenal, 0.06 g of catalyst, 24 h, atmospheric pressure.

Al_2O_3 and MgO, at 50°C. The graphite showed similar activity to silicon carbide in the oxidation of 2-hexenal. Overall, the MnO_2 support showed the highest activity and selectivity for 2-hexenoic acid. Therefore, Au/MnO_2 (1 wt.%) catalyst was used for further studies. An XRD pattern of MnO_2 and Au/MnO_2 catalyst is shown in Figure 1. Comparison with pure support reveals that most of the reflections stem from the support. The main reflections of gold are expected at 2θ = 38.1803° (100%), 44.4° (52%), 64.6° (32%), and 77.4° (36%), while the reflection of MnO_2 phase can be identified by the major peaks at 28.88°, 37.4°, 42.62°, 56.65°, 59.10°, 64.96°, 67.15°, and 72.30°.

The oxidation of 2-hexenal was analyzed using MnO_2-supported Au catalyst (Au/MnO_2) atmospheric air at a wide range of temperatures (Figure 2). It can be observed that an increase in the temperature led to a significant increase in the oxidation of 2-hexenal. The selectivity data for 2-hexenal oxidation at four different reaction temperatures (50–80°C) is also shown in Figure 2. Increase in the reaction temperature is associated with a slight decrease in the selectivity for 2-hexenoic acid. This may be due to the catalyst-facilitated dimerisation of the oxidation product 2-hexenal to 4,6-dipropyl-3,4,5,6-tetrahydropyran-2-one-5-carboxaldehyde via the Diels-Alder reaction [20].

For the oxidation of alcohols, the activity of gold catalysts can be increased by alloying gold with another metal [21, 22]. Table 2 compares the activity of MnO_2-supported Au, Pd, and Au-Pd catalysts for 2-hexenal oxidation under solvent-free conditions using oxygen from air. The highest conversion was observed when using the bimetallic catalyst, while the Pd catalyst showed the lowest activity. It is clear that the bimetallic catalysts have a synergistic effect, as the catalytic activity was higher than the corresponding monometallic catalysts at 50°C. In addition, it was observed that monogold gave a higher conversion rate, compared to Pd only. These results are in accordance with the previous studies on the redox reactions, namely, the oxidation of primary alkyl alcohols [21] and the synthesis of H_2O_2 from H_2 oxidation [23], whereby very pronounced synergistic effects on activity and selectivity were found.

TABLE 2: Effect of bimetal on 2-hexenal oxidation.

Catalyst	Conversion%	Selectivity%	
		Dimer	2-Hexenoic acid
Au/MnO_2	81.3	8.3	89.1
$Au\text{-}Pd/MnO_2$	83.3	8.0	89.9
Pd/MnO_2	73.6	7.5	89.2

Reaction conditions: 4.23 g of 2-hexenal, 0.06 g of catalyst, 50°C, 24 h, atmospheric pressure.
Dimer: 4,6-dipropyl-3,4,5,6-tetrahydropyran-2-one-5-carboxaldehyde.

TABLE 3: Effect of preparation methods on 2-hexenal oxidation using 1% Au/MnO_2.

Method	Conversion%	Selectivity%	
		Dimer	2-Hexenoic acid
Sol	81.3	8.3	89.1
Impregnation	76.1	7.8	89.1
DP	77.6	6.2	90.3

Reaction conditions: 4.23 g of 2-hexenal, 0.06 g of catalyst, 50°C, 24 h, atmospheric pressure.
Dimer: 4,6-dipropyl-3,4,5,6-tetrahydropyran-2-one-5-carboxaldehyde.

The preparation method is a commonly used parameter with regard to affecting the catalyst activity [24]. SI method, DP method, and the impregnation method (IM) were used to prepare 1% Au/MnO_2 and the activities were summarized in Table 3. Catalysts prepared by impregnation and DP showed similar activities. However, catalyst prepared by SI method showed enhanced activity, which may be due to the much smaller gold nanoparticle size and its higher dispersion [25]. The particle size distributions for Au/MnO_2, prepared using SI, DP, and IM, are shown in Figure 3. It is apparent

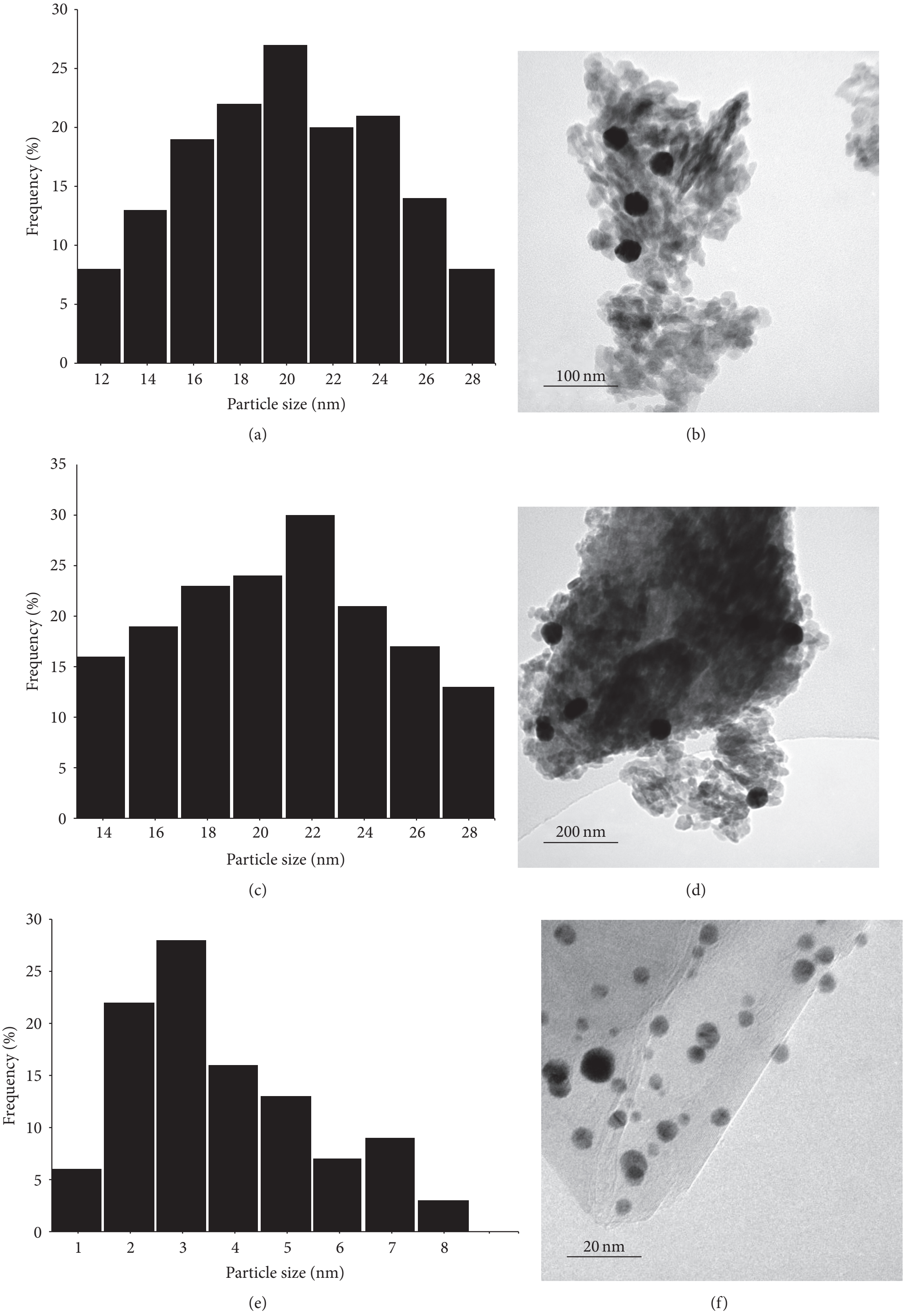


Figure 3: Particle size distributions and TEM image of Au/MnO_2 using different preparation methods, respectively: DP (a) and (b); IM (c) and (d); SI (e) and (f).

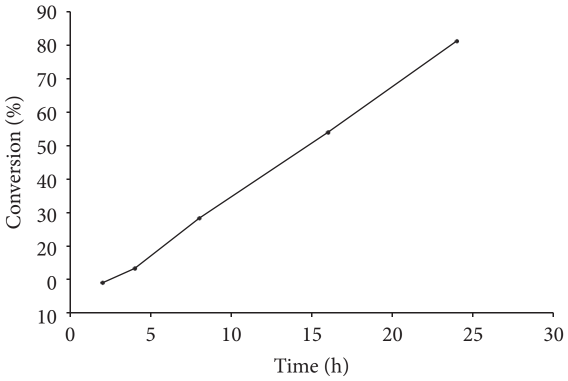


Figure 4: Effect of reaction time for the conversion of 2-hexenal using Au/MnO_2. Reaction conditions: 4.23 g of 2-hexenal, 0.06 g of catalyst, atmospheric pressure.

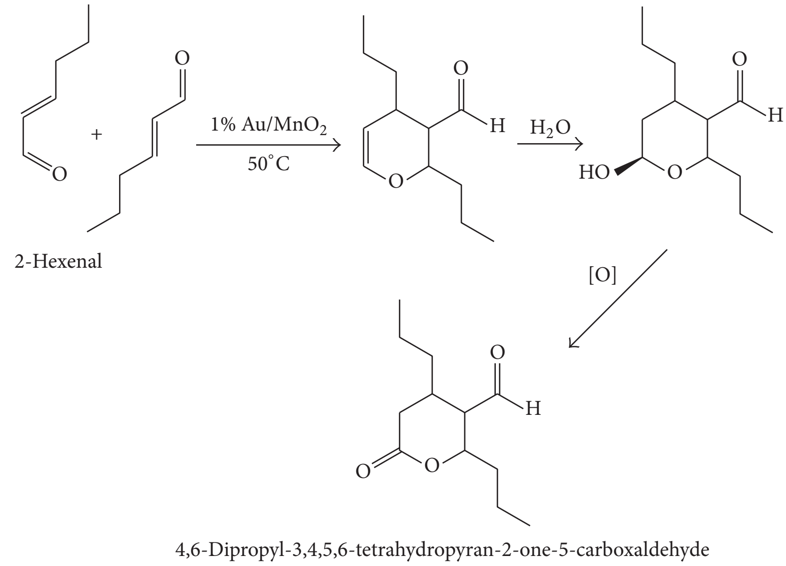


Figure 5: Diels-Alder formation of product 4,6-dipropyl-3,4,5,6-tetrahydropyran-2-one-5-carboxaldehyde from oxidation product 2-hexenal.

that the DP and IM show very similar distribution, which is in accordance with the activity for those two catalysts. Figure 3 showed the particle size distribution of the catalysts prepared by DP and IM (10–30 nm). This is consistent with the activities of the gold catalysts that were prepared by DP and IM, which gave the same activity, as shown in Table 3. In contrast, the particle size distribution of the catalyst prepared using the SI method comprises much smaller particles with the diameter of 2-3 nm. This gave the catalysts enhanced activity, possibly due to higher dispersion of much smaller gold nanoparticles, as shown in Figure 3. Several previous studies [19–22] noted that gold catalyst activity has an inverse relationship with the gold particle size. These results suggest that SI can be used to prepare effective catalysts of this type with regard to 2-hexenal oxidation.

Figure 4 showed the results of time online study of the 2-hexenal oxidation, which was performed using the optimized 1% Au/MnO_2 SI catalyst. Under optimal conditions, there was a steady increase in 2-hexenal oxidation with reaction time. This increase was linear, indicating that there was no apparent deactivation of the catalysts in this reaction under our conditions. Table 4 shows that the selectivity for carboxylic acids was observed at the beginning of the reaction. However, the selectivity for carboxylic acids decreased with increasing time, indicating that the partial oxidation of 2-hexenal is stable for a short time. In contrast, the selectivity for 4,6-dipropyl-3,4,5,6-tetrahydropyran-2-one-5-carboxaldehyde (dimer) increased with increasing time. The catalyst may facilitate the dimerisation of the oxidation of 2-hexenal to the dimer via the Diels-Alder reaction [20], as shown in Figure 5. This was previously reported by Hutchings et al. who found that a dimer could be formed by formal Diels-Alder dimerisation of crotonaldehyde.

In conclusion, the present study showed that gold-supported catalysts were an effective catalyst for 2-hexenal oxidation under green reaction conditions. Gold nanoparticles supported on MnO_2, CeO_2, SiC, graphite, MgO, Al_2O_3, and TiO_2 exhibited different activities in 2-hexenal oxidation,

Table 4: Effect of reaction time on the selectivity during the oxidation of 2-hexenal using 1% Au/MnO_2.

Reaction time	Selectivity%	
	Dimer	2-Hexenoic acid
2 h	3.5	95.2
4 h	4.4	94.1
8 h	4.8	94.0
16 h	5.3	92.3
24 h	8.3	89.1

Reaction conditions: 4.23 g of 2-hexenal, 0.06 g of catalyst, 50°C, atmospheric pressure.
Dimer: 4,6-dipropyl-3,4,5,6-tetrahydropyran-2-one-5-carboxaldehyde.

as follows: MnO_2 > graphite > CeO_2 > SiC > TiO_2 > Al_2O_3 > MgO. Therefore, it was concluded that MnO_2 was the support of choice. The oxidation pathway was the main reaction under almost all conditions. Furthermore, it was shown that a significant amount of the dimer arose from a dimerisation reaction. The highest activity of gold catalysts was obtained when SI method was used for catalyst preparation, which gave smaller gold nanoparticles.

Competing Interests

The author declares that there are no competing interests regarding the publication of this paper.

Acknowledgments

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