

Article

Boosting Solvent-Free Aerobic Oxidation of Benzylic Compounds into Ketones over Au-Pd Nanoparticles Supported by Porous Carbon

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Abstract: The exploitation of highly efficient solvent-free catalytic systems for the selective aerobic oxidation of benzylic compounds to produce corresponding ketones with molecular oxygen under mild conditions remains a great challenge in the chemical industry. In this work, Au-Pd nanoparticles supported on porous carbon catalysts were fabricated by the borax-mediated hydrothermal carbonization method and the chemical reduction method. The physicochemical properties of Au-Pd bimetallic samples were examined by XRD, N₂ sorption, SEM, TEM, and XPS techniques. The Au-Pd nanoparticles have successfully immobilized on the spherical carbon support with a porous structure and large surface area. A solvent-free catalytic oxidation system was constructed to selectively convert indane into indanone with Au-Pd nanocatalysts and O₂. In contrast with a monometallic Au or Pd catalyst, the resulting bimetallic Au-Pd catalyst could effectively activate O₂ and exhibit improved catalytic activity in the controlled oxidation of indane into indanone under 1 bar O₂. A total of 78% conversion and >99% selectivity toward indanone can be achieved under optimized conditions. The synergistic effect of Au and Pd and porous carbon support contributed to the high catalytic activity for aerobic benzylic compound oxidation. This work offers a promising application prospect of efficient and recyclable Au-Pd nanocatalysts in functional benzylic ketone production.

Keywords: solvent free; Au-Pd nanoparticles; porous carbon; molecular oxygen; selective oxidation



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1. Introduction

The transformation of benzylic compounds into ketones is significant in producing value-added chemicals and intermediates in the chemical industry [1,2]. Traditionally, stoichiometric amounts of oxidants (e.g., Cr₂O₃, KMnO₄, I(III), or Se(IV)) [3,4] and various homogeneous catalysts (e.g., cobalt(II) salts combined with N-hydroxyphthalimide (Co(II)-NHPI), Fe(NO₃)₃, Pd, Pt, Ir, or Ru complexes) have been employed for the oxidation of benzyl compounds [5]. Yet, these methods suffer from serious drawbacks, such as excessive use, difficult separation, and recovery, as well as a lack of reuse of these reagents or catalysts [6–8]. To overcome the above problems, substantial endeavors have been devoted to developing more environmentally heterogeneous catalytic systems for the selective oxidation of benzyl compounds [9–13]. Various catalysts, including MnO₂@Fe₃O₄ nanoparticles [10], Cu₃(PO₄)₂ [11], LaMO₃ (M = Cr, Co, Fe, Mn, Ni) perovskites [12], and Cr/MCM-41 [13], have been explored for the oxidation of the C–H bonds of benzyl compounds by combining with oxidants. In general, these catalytic systems still required a large amount of toxic or volatile organic solvents (e.g., ethanol, acetonitrile, dichloromethane, and chlorobenzene) and various oxidants (e.g., alkyl hydroperoxide, hydrogen peroxide (H₂O₂),

and iodosobenzene) [12–16]. This would result in difficulty in product separation and purification, increasing energy consumption, and generating lots of poisonous and harmful wastewater in the production processes. In contrast, utilizing air or molecular oxygen as a sustainable oxidant, the aerobic oxidation of benzyl compounds in a solvent-free system is an ideal alternative to the above systems, and it promises to be a cost-efficient, low-energy consuming, and green oxidation process for the production of benzylic ketones [17].

Because of the inertness of C–H bonds, it is difficult to activate molecular oxygen to oxidize benzyl compounds under mild conditions. Moreover, due to the higher reactivity of target products than benzyl compounds, it is also difficult to control the reaction process to avoid overoxidation and obtain a single ketone product [18]. Therefore, to overcome the great challenge in the activation of molecular oxygen at mild conditions, it is urgent to develop an efficient catalyst with high stability for benzylic C–H bond oxidation with O₂. In the most reported aerobic oxidation systems, additional radical initiators (e.g., NHPI or *tert*-butyl hydroperoxide) [19] or harsh reaction conditions (e.g., high temperature, high O₂ pressure) were needed to activate O₂ and oxidize benzylic compounds [20]. Only a few catalysts, such as MnCeO_x, Cu-Pd alloy nanoparticles, and Au@ZnO, were applied for the aerobic oxidation of benzylic compounds without additional radical initiators [21–23]. Nevertheless, the efficient transformation of benzyl compounds with high yields of ketones remains a great challenge.

Indane, as a representative benzylic compounds, is present in many vital biological and medicinal systems [24]. Indanone, as the main product of indane oxidation, is an important intermediate for a variety of fine chemicals, such as pharmaceuticals, agrochemicals, and dyes [25]. Monometallic Au or Pd nanoparticles supported catalysts that have exhibited good catalytic activity for the controlled indane oxidation. For instance, Dapurkar et al. [26] applied various supported gold nanoparticles for the selective indane oxidation at 1 atm O₂ and attained a high selectivity (90%) at moderate conversion (46%) in the presence of Au/TiO₂. Liu et al. [22] developed novel Au@mZnO catalysts for the aerobic oxidation of indane and displayed good catalytic activity with high conversion (88.5%) and moderate selectivity toward indanone (60%) under 120 °C, 1 bar O₂, and 20 h. Zhang et al. [27] reported that indane could be oxidized by 4%Pd@C-Glu_A-550 with 98% selectivity toward 1-indanone at 31.2% conversion without the addition of other solvent and organic ligands under mild reaction conditions (120 °C, 1 atm air, 11 h). However, the catalytic efficiency for the selective oxidation of indane to indanone by single-loading Au or Pd nanoparticles needs to be further enhanced in the solvent-free system without the addition of any organic ligands or promoters. Herein, it is desirable to develop novel Au-based nanocatalysts with low metal loading to efficiently realize indane transformation into indanone with O₂ under mild conditions.

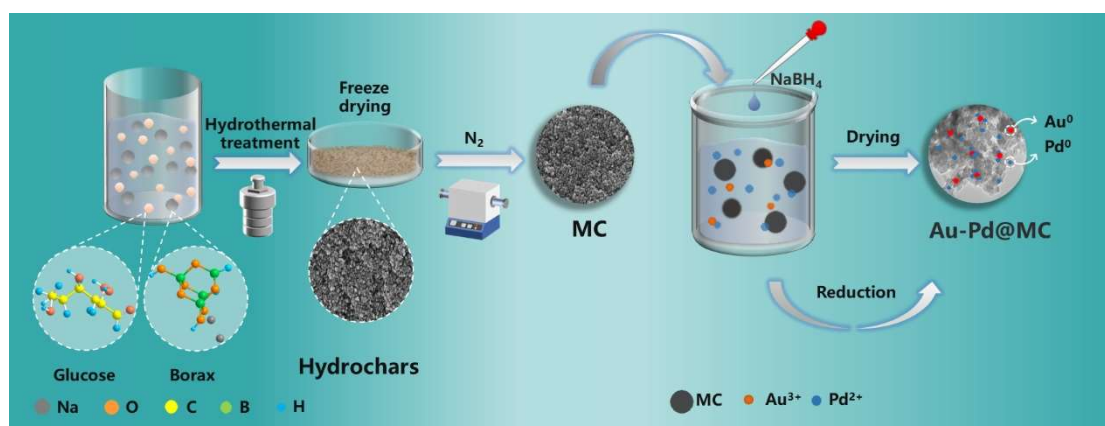
It is known that the introduction of a second metal into Au catalysts is an effective strategy to ameliorate the O₂ activation ability and the catalytic oxidation activity of single metal catalyst via enhancing the catalytically active sites [20,28,29]. Bimetallic Au-Pd catalysts have attracted great attention because of excellent catalytic activity in many oxidation reactions [28,30]. Yet, seldom works relating to supported Au-Pd nanocatalysts for the aerobic oxidation of benzylic compounds into ketones in solvent-free systems were reported. In this work, we developed a facile and environmentally friendly method for fabricating Au-Pd loading porous carbon catalysts (Au-Pd/MC) by combining the hydrothermal carbonization of glucose and a chemical reduction process. Borax (Na₂B₄O₇) was used as a structure-directing agent to construct spherical carbon with a hierarchically porous structure, which would afford abundant oxygen-containing functional groups to anchor Au-Pd nanoparticles [27,31]. These catalysts were applied for the solvent-free catalytic oxidation of benzylic compounds into ketones with O₂ under mild conditions. Indane was selected as a typical benzylic compound to evaluate the catalytic activity of Au-Pd bimetallic catalysts, with monometallic Au or Pd catalysts as a comparison. The influence of Au/Pd ratios, reaction time, and reaction temperature on the catalytic activity for the oxidation of indane were studied in detail. A total of 78% conversion of indane and

>99% selectivity toward indanone could be achieved at the optimal conditions. A possible reaction pathway was proposed for the aerobic oxidation of indane into indanol and indanone over the Au-Pd catalyst. Overall, this work would contribute to the advancement of efficient catalyst design for aerobic oxidation to produce fine chemicals.

2. Results

2.1. Characterization of the Catalyst

The Au-Pd/MC catalysts were fabricated by a simple method containing borax-mediated hydrothermal carbonization and a chemical reduction process. Scheme 1 displays the preparation procedure of Au-Pd catalysts. The first step involved borax-mediated hydrothermal carbonization of glucose at 200 °C. Borax was added as a structure-directing agent to control the morphology and particle diameters of carbonaceous material [27]. Due to the buffer effect of the borax additive, borax would help rapid nucleation and slow the growth of carbonaceous particles. As a result, spherical hydrochars with a uniform size of about 20 nm were formed during the hydrothermal carbonization process (Figure S1). Then, the obtained hydrochars were further pyrolyzed at 550 °C under an N₂ atmosphere to improve the graphitization degree and retain plentiful oxygen-containing functional groups [32,33]. Moreover, a large number of small molecular gases (e.g., CO, CO₂, and H₂O) were released to generate many pores during this carbonization process [34]. Therefore, spherical carbon with a porous structure and rich porosity was obtained. The second step involved the loading of Au-Pd nanoparticles on the surface of as-prepared porous carbon materials by a chemical reduction process. NaBH₄ was used as a reducing agent to synthesize bimetallic Au-Pd/MC catalysts. Unless noted otherwise, the loading total metal content was 1% and the Au/Pd mass ratio was 1:3 in this work.



Scheme 1. Preparation procedure of the Au-Pd/MC catalyst.

Figure 1 shows the XRD patterns of the Au-Pd/MC sample with Au/MC, Pd/MC, and MC as a comparison. All the samples had two broad peaks at 21.4 and 42.8°, which belonged to amorphous carbon [35,36]. The intensity of carbon peaks reduced after metal loading, which was caused by the partial coverage of the carbon surface by metal nanoparticles. Apart from the carbon peaks, the diffraction peaks at 38.2, 44.4, 64.6, and 77.6° in Au/MC can be indexed as (111), (200), (220), and (311) planes of metallic Au⁰ [37]. For the Pd/MC sample, the diffraction peaks at 40.1, 46.7, and 68.2° could be attributed to (111), (200), and (220) planes of Pd⁰, while the diffraction peaks at 27.3 and 31.7° could be assigned to (200) and (220) planes of PdO particles, respectively [38,39]. In contrast with monometallic Au/MC and Pd/MC catalysts, these peaks of metallic Au, metallic Pd, and PdO were all observed in bimetallic Au-Pd/MC. Upon careful observation, the intensity of Pd and PdO peaks in Au-Pd/MC were weaker and broader than those of the monometallic Pd/MC catalyst, revealing the smaller sizes of metal and metal oxide particles in the bimetallic catalyst [40]. These results implied the formation of Au-Pd nanocomposites.

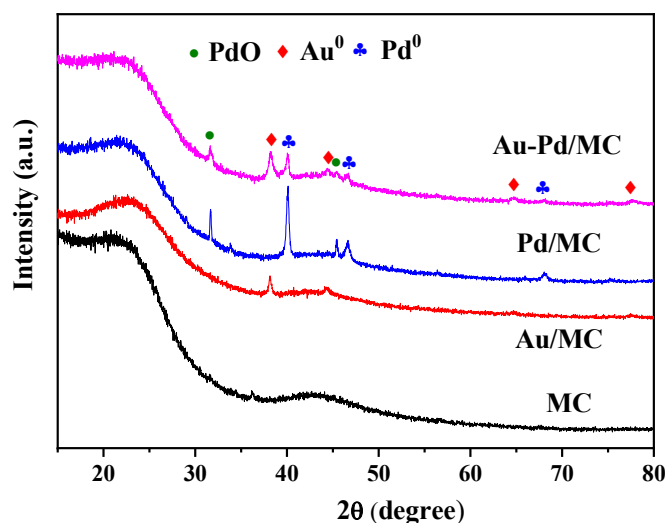


Figure 1. XRD patterns of various catalysts.

Nitrogen sorption isotherms were conducted to analyze the porous structure of Au-Pd/MC and MC, and the results are shown in Figure 2. Typical type-IV isotherms were observed in both MC and Au-Pd/MC [41]. The presence of hysteresis loops at a relative pressure of 0.2–0.8 implied a mesoporous character in both samples [34]. Both Au-Pd/MC and MC displayed considerable N_2 adsorption at a low pressure lower than 0.1, indicating rich microporosity. The N_2 adsorption amount at both low pressure and medium pressure slightly decreased after metal loading, indicating the smaller surface area and porosity of Au-Pd/MC. This was possibly caused by the blockage of pores by the metal nanoparticles. The pore size distributions (Figure 2b), determined by the density functional theory (DFT) model, supported the well-defined micro-mesopore size distribution in both Au-Pd/MC and MC. Table 1 illustrates the calculated specific surface areas (S_{BET}) and pore volumes. The S_{BET} and total pore volume (V_{total}) of the MC sample were $485 \text{ m}^2 \text{ g}^{-1}$ and $0.26 \text{ cm}^3 \text{ g}^{-1}$, respectively. Wherein, the micropore volume (V_{micro}) accounted for 64%. The high S_{BET} and appropriate pore diameter of MC afforded promising support for catalysts. In contrast, S_{BET} decreased slightly after loading metallic nanoparticles, and it remained at a considerable S_{BET} value of $>410 \text{ m}^2 \text{ g}^{-1}$ and a high V_{total} of $>0.18 \text{ cm}^3 \text{ g}^{-1}$, suggesting that most of the pores were accessible. It was worth noting that the proportion of V_{micro} increased to 78.9% in Au-Pd/MC, implying that Au-Pd nanoparticles preferred to anchor on the mesoporous surface of carbon material.

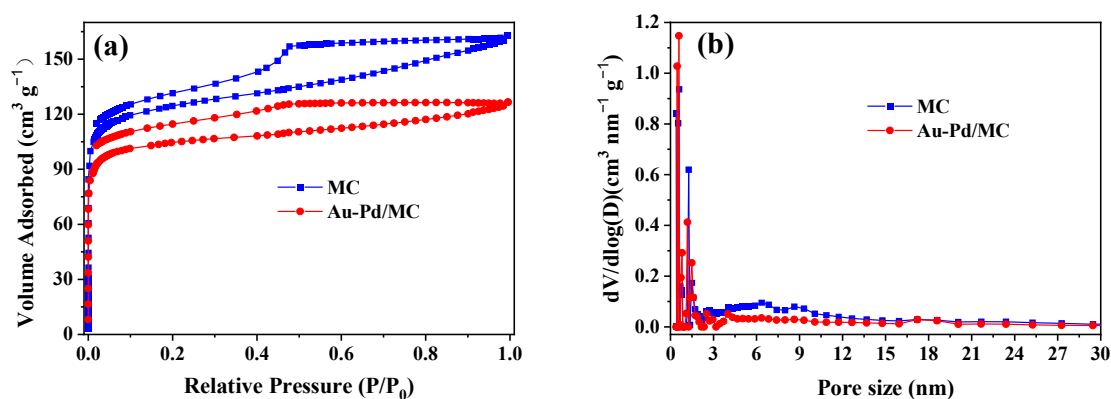
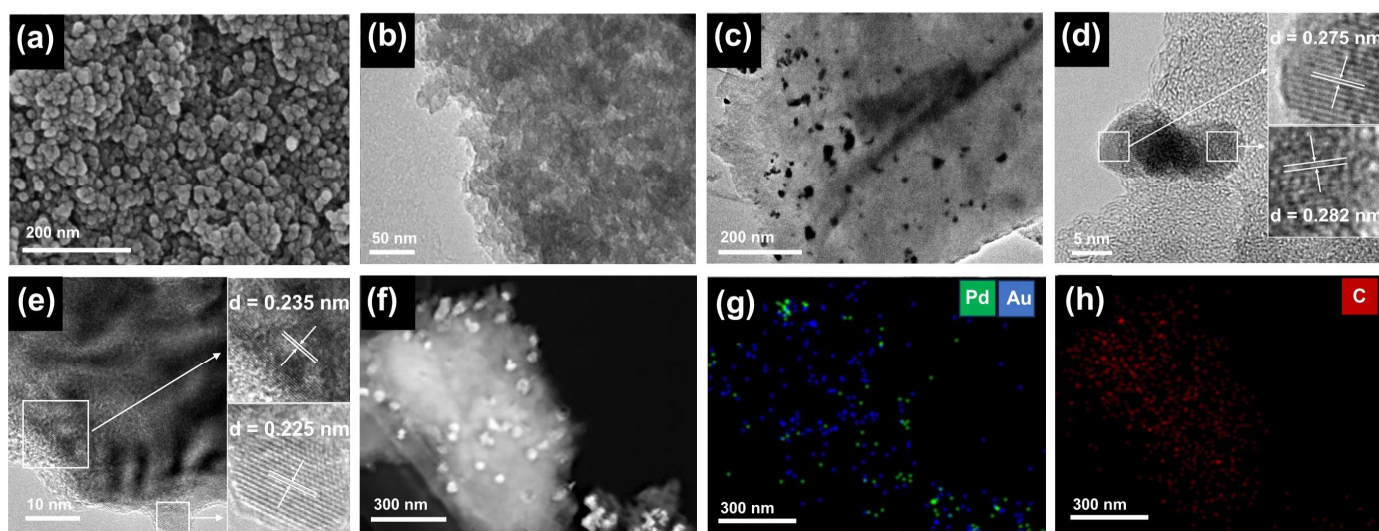


Figure 2. N_2 sorption isotherms at 77 K (a) and pore size distributions (b) of MC and Au-Pd/MC.

Table 1. Porous properties of representative catalysts.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)
MC	485	0.25	0.16	0.07
1%Au/MC	415	0.20	0.14	0.04
1%Pd/MC	413	0.18	0.15	0.05
1%Au-Pd/MC	419	0.19	0.15	0.04

The morphology of the carbon-supported catalysts was characterized via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figures S1 and 3a illustrate the SEM images of the hydrochar and MC support. The morphological feature of the hydrochar was a spherical structure with a uniform size of about 20 nm. The spherical carbon particles retained well after carbonization at 550 °C. The TEM image of MC, shown in Figure 3b, supported well-dispersed spherules with a hierarchical porous structure, which was beneficial for heterogeneous catalytic reactions. Figure 3c exhibits the metal particle distributions in Au-Pd/MC. Au-Pd nanocomposites with particle sizes in the range of 5–35 nm dispersed on the carbon support. The HRTEM images, shown in Figure 3d, displayed that the lattice spacings at 0.275 nm and 0.282 nm related to AuO_x and PdO particles, respectively [42]. The lattice spacings at 0.225 nm and 0.235 nm were also observed in Figure 3e, which were assigned to the (111) facet of metallic Pd^0 and the (111) facet of metallic Au^0 , respectively [43]. The results confirmed the existence of bimetallic nanocomposites on the carbon support. The corresponding mapping of Au-Pd/MC further supported the good distribution of Au and Pd nanoparticles on the carbon support. The average sizes of Au^0/AuO_x and Pd^0/PdO particles were about 15.9 and 6.9 nm, respectively (Figure S2), which were a bit smaller than the values predicted by XRD. It was inferred that the Au-Pd nanocomposites have successfully immobilized on the porous spherical carbon support.

**Figure 3.** (a) SEM image of MC, TEM images (b) of MC and (c) Au-Pd(1:3)/MC, (d,e) HRTEM images of Au-Pd/MC, and (f–h) the corresponding mapping images of elemental Pd, Au and C.

XPS spectra were also measured to investigate the surface chemical composition and chemical state of Au-Pd/MC, with a monometallic catalyst as a comparison. Au-Pd/MC mainly had four elements: C, O, Au, and Pd. As shown in Figure 4a, there were four types of carbon in carbon-supported samples, including the C–C group at 284.6 eV, the C–O group at 286.3 eV, the C=O group at 288.1 eV, and the COOR group at 289.7 eV [44,45]. Compared to Au/MC, the C–O and C=O peaks of Pd/MC and Au-Pd/MC shifted 0.3–0.5 V toward higher binding energy. Due to the difference in electronegativity between Au and

Pd, the shift of C–O and C=O peaks might relate to the reduction in the electron density of adjacent C atoms by the formation of Au–O or Pd–O bonds [34]. As displayed in Figure 4b, the O 1s XPS spectra of Au/MC catalysts can be grouped into three peaks at 532.3, 533.5, and 535.3 eV, assignable to lattice oxygen species (O_{lat}), surface adsorbed oxygen species (O_{sur}), and surface hydroxyl species (O_{OH}), respectively [46,47]. Similarly, three peaks were observed in Pd/MC and Au-Pd/MC, except that the O_{sur} peak shifted 0.1–0.2 eV toward higher binding energy, supporting the formation of Au–O or Pd–O bonds. As shown in Table S1, the concentrations of surface oxygen in the Au/MC, Pd/MC, and Au-Pd/MC samples, calculated by XPS, were 13.3 at%, 12.3 at%, and 13.8 at%, respectively. The result confirmed the presence of abundant oxygen-containing functional groups on the carbon surface. The component proportion of O_{lat} , O_{sur} , and O_{OH} in the Au-Pd/MC was 18.8%, 34.2%, and 47.0% in the total O atoms, respectively. O_{sur} might serve as the primary anchoring site to bond Au-Pd nanocomposites.

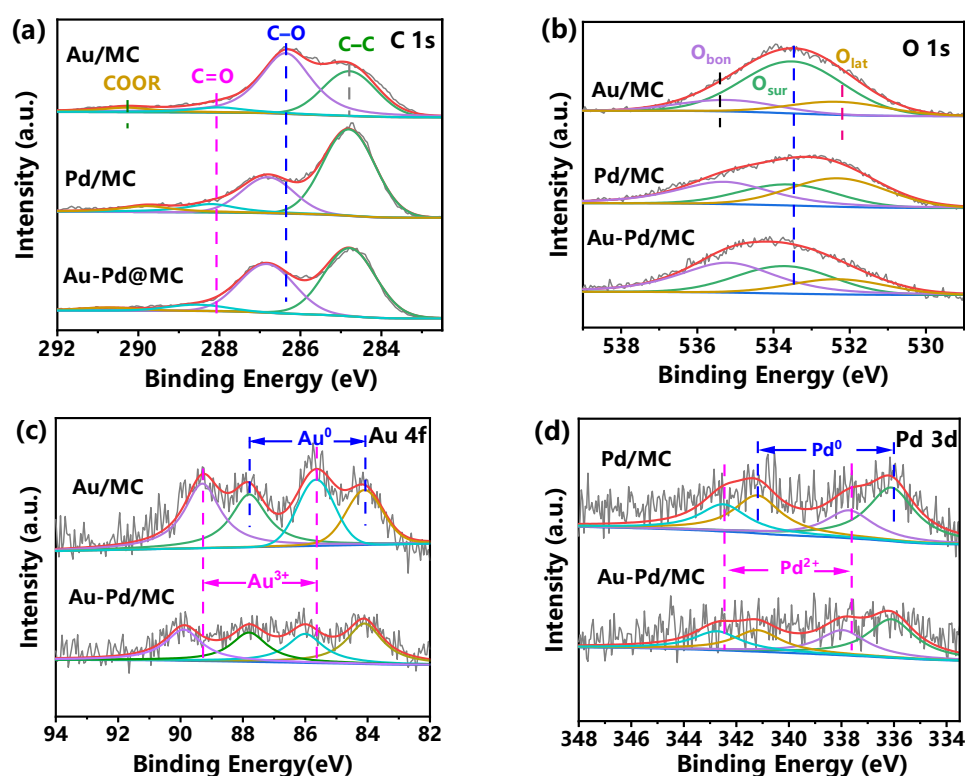


Figure 4. XPS spectra of (a) C 1s, (b) O 1s, (c) Au 4f, and (d) Pd 3d for various catalysts.

As shown in Figure 4c, the Au 4f XPS spectra could be fitted into four peaks, attributable to Au 4f 7/2 and Au 4f 5/2 core levels. The Au 4f 5/2 peaks in the Au/MC sample were around 87.8 and 89.3 eV, while the Au 4f 7/2 peaks were at around 84.1 and 85.6 eV. The double peaks at 84.1 and 87.8 eV related to metallic Au, while the other double peaks at 85.6 and 89.3 eV belonged to Au^{3+} [30]. The results indicated the presence of metallic Au and Au^{3+} . As shown in Figure 4d, the Pd 3d XPS spectra consisted of four peaks, corresponding to Pd 3d 5/2 and Pd 3d 3/2. The double peaks at around 336.1 and 341.2 eV in Pd/MC were attributed to Pd^0 , while the other double peaks at around 337.7 and 342.5 eV were associated with Pd^{2+} [48]. Compared to monometallic Au/MC and Pd/MC samples, there was no shift in the Au^0 and Pd^0 peaks for Au-Pd/MC, while the Au^{3+} and Pd^{2+} peaks in Au-Pd@MC were shifted to higher binding energies by 0.2–0.6 eV. These shifts probably originated with the generation of Au-Pd bimetallic nanocomposites. Furthermore, the concentrations of surface Au and Pd in the Au-Pd/MC sample were 0.04 at%, and 0.24 at%, respectively. The component proportion of Au^0 in the total Au atoms increased from 46.1% in Au/MC to 53.7% in Au-Pd/MC, while the component

proportion of Pd⁰ in the total Pd atoms reduced from 62.4% in Pd/MC to 57.7%. These results supported the presence of Au⁰, Pd⁰, AuO_x, and PdO nanocomposites in Au-Pd/MC.

The NH₃-TPD measurement was performed to analyze the acid properties of the MC and Au-Pd/MC samples. Figure 5 displays the NH₃-TPD profiles of various samples. The NH₃ desorption profile of both MC and Au-Pd/MC exhibited a strong peak in the 100–400 °C range and a weak peak in the 400–600 °C range. The former peak was attributed to oxygen-containing groups, like C=O and OH, while the latter peak was assigned to medium to strong acid sites on the surface of carbon-based material. The loading of Au-Pd nanoparticles had little effect on the weak acid sites but slightly reduced the medium to strong acid sites, probably originating from the partial coverage of carbon by metal species. The abundant acid sites in Au-Pd/MC might be favorable to the contact between the catalyst and C–OH bond in the intermediates, thereby improving the yield of ketones.

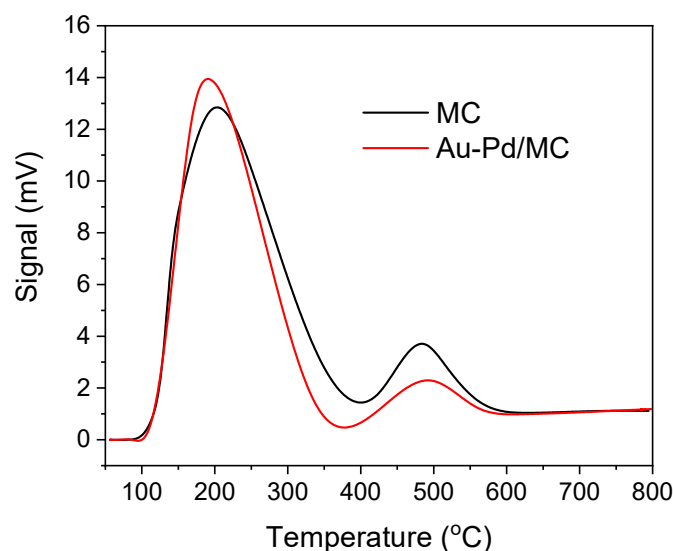


Figure 5. NH₃-TPD profiles of MC and Au-Pd/MC.

2.2. Catalytic Performance of the Catalyst

The catalytic performances of bimetallic catalysts were evaluated for selective oxidation of indane with O₂ as the oxidant. The aerobic oxidation of indane was conducted in a solvent-free system at 1 bar of O₂. As shown in Table 2, there was little catalytic activity in the blank system or MC system for 4 h at 100 °C (Entries 1 and 2), indicating that indane could not undergo self-oxidation under 1 bar O₂ or in the presence of MC support and 1 bar O₂. Under similar reaction conditions, 1.5% and 1.9% of indane were converted with 1%Pd/MC and 1%Au/MC as the catalysts, suggesting that Pd and Au-based catalysts were capable of activating O₂ and oxidized indane in the presence of atmospheric oxygen and low reaction temperature, even if catalytic efficiency was low (Entries 3 and 4). On a positive note, the activity was boosted with the introduction of Au-Pd nanocomposites. 3% of indane was transformed with the Au-Pd(1:3)/MC catalyst, accompanied by the formation of indanone and indanol (Entry 5). When the reaction proceeded at 120 °C and 4 h under the atmospheric pressure of O₂, the conversion of Au-Pd(1:3)/MC enhanced to 65%, with 38% of indanol selectivity and 62% of indanone selectivity (Entry 11). Extending the reaction time to 8 h and 24 h, the residual indane could continue to be oxidized, and the indanol intermediate was completely converted into indanone. As a result, the highest activity with 76% conversion and >99% indanone selectivity could be obtained with Au-Pd(1:3)/MC (Entries 12 and 13). The result revealed that Au-Pd/MC was highly effective in activating O₂ under atmospheric pressure to controllably transform benzylic compounds into ketones. It was also worth noting that Au-Pd/MC had a higher catalytic performance than those of most other types of catalysts for the solvent-free aerobic oxidation of indane into indanone at 1 bar O₂ without the addition of any organic ligands

or promoters (Table S2). To study the impact of carbon support on catalytic performance, the catalytic efficiency of 1%Pd/MC and 5%Pd/commercial C have been investigated and compared for the aerobic oxidation of indane. It was found that 1%Pd/MC had slightly higher activity than that of 5%Pd/commercial C (Entries 6 and 10), which suggested that micro/mesoporous carbon support could significantly reduce the usage of noble metal but maintain its high activity. The result testified that micro/mesoporous carbon could play a vital role in the aerobic oxidation of indane.

Table 2. Oxidation of indane catalyzed by various catalysts with O₂.

Entry	Catalyst	t (h)	T (°C)	Conversion (%)	Selectivity (%)	
						
1	without catalyst	4	100	0	-	-
2	MC	4	100	0	-	-
3	1%Pd/MC	4	100	1.5	60	40
4	1%Au/MC	4	100	1.9	55	45
5	Au-Pd(1:3)/MC	4	100	3	46	54
6	1%Pd/MC	4	120	30	46	54
7	1%Au/MC	4	120	55	42	58
8	1%Au/MC	8	120	60	59	41
9	1%Au/MC	12	120	64	72	28
10	5%Pd/C	4	120	28	56	44
11	Au-Pd(1:3)/MC	4	120	65	38	62
12	Au-Pd(1:3)/MC	8	120	71	8	92
13	Au-Pd(1:3)/MC	24	120	76	0	>99

Reaction conditions: 4 mL indane, 20 mg catalyst, 1 bar O₂.

Under 120 °C and 1 bar of O₂ for 8 h, the catalytic activity of Au-Pd/MC catalysts with different Au/Pd mass ratios (1:1, 1:2, 1:3, 1:4) was tested by the aerobic oxidation of indane. Figure 6 displayed that by elevating the Au/Pd mass ratio from 1:1 to 1:3, both the conversion and indanone selectivity gradually improved. The highest activity of Au-Pd/MC, with 71% conversion and 92% indanone selectivity, could be obtained when the Au/Pd mass ratio was 1:3. A negative effect on indanone yield appeared when the ratio was 1:4. It was concluded that the Au/Pd ratio had a great impact on the transformation of indane as well as indanone selectivity. These results supported the synergistic effect in the Au-Pd/MC catalyst. Hence, the Au/Pd mass ratio of Au-Pd/MC is decided as 1:3 in this work. The influence of reaction temperature on the catalytic activity was also studied using the optimized Au-Pd catalyst. As shown in Figure 7, when the reaction proceeded at 80 °C, indane was hard to convert. The indane conversion and indanone selectivity were remarkably enhanced by increasing the temperature up to 120 °C. Further, by increasing the reaction temperature to 140 °C, the indane conversion was slightly reduced. Therefore, the optimized reaction temperature for the catalytic oxidation system was 120 °C.

As the reusability of the catalyst is a vital factor for industrial application, the recycling test of Au-Pd/MC was examined to ensure that the bimetallic catalyst could be reused and maintain good activity. After each run of the reaction, Au-Pd/MC was separated, washed completely, dried, and reused in the next run. As shown in Figure 8, no apparent decrease in the catalytic activity was found during the five runs, confirming the good stability and reusability of the Au-Pd/MC catalyst in the aerobic oxidation of indane. The used catalyst after the reaction was also measured by XPS, and the results are shown in Figure S3. There was no obvious change in the Pd 3d spectra, while a higher Au³⁺/Au⁰ ratio was found in the Au 4f spectra for the used Au-Pd/MC, indicating that partial Au⁰ in the fresh sample was oxidized during the reaction. The slight decrease in catalytic activity after the fifth recycle might be attributed to the decreased Au⁰ in the used Au-Pd/MC.

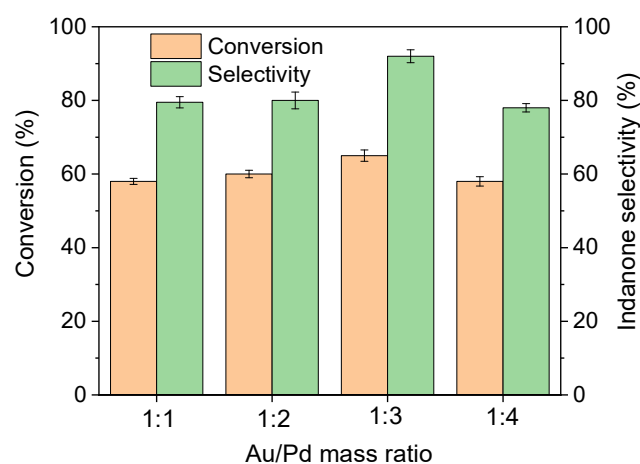


Figure 6. The catalytic activities of Au-Pd/MC samples with different Au/Pd mass ratios. Reaction conditions: 4 mL indane, 20 mg catalyst, 1 bar O₂, 120 °C, 8 h.

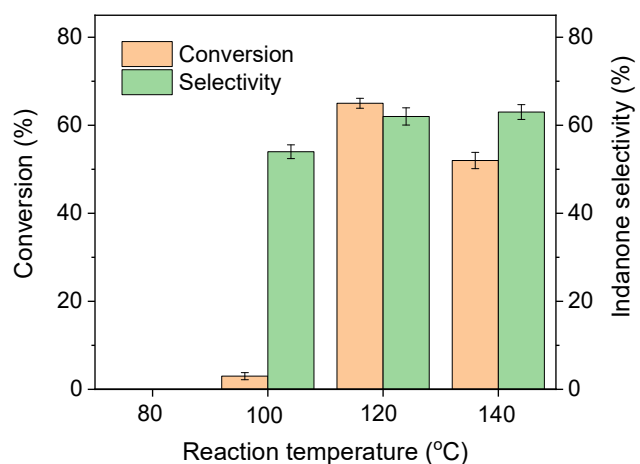


Figure 7. The catalytic activities of Au-Pd/MC samples at different reaction temperatures. Reaction conditions: 4 mL indane, 20 mg catalyst, 1 bar O₂, 4 h.

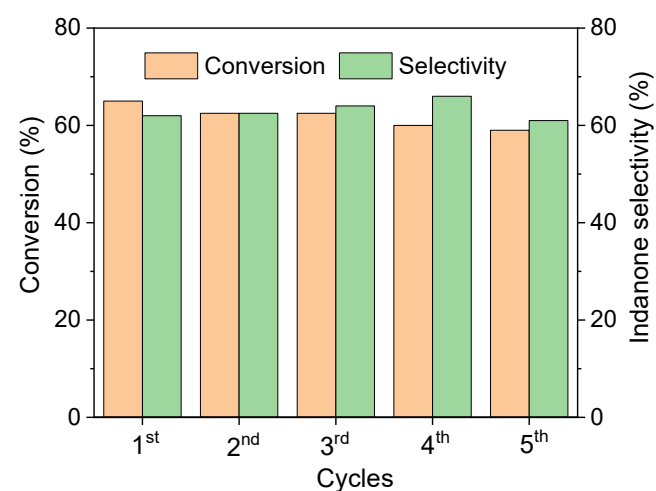
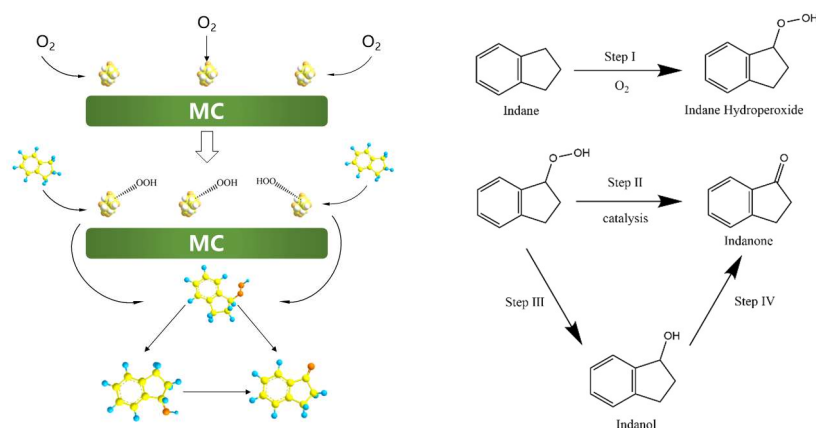


Figure 8. Reuses of the Au-Pd/MC catalyst in the solvent-free oxidation of indane. Reaction conditions: 4 mL indane, 20 mg catalyst, 1 bar O₂, 120 °C, 4 h.

2.3. Reaction Pathway

In view of these results, a possible reaction pathway was proposed for the aerobic oxidation of indane into indanol and indanone over the Au-Pd/MC catalyst. It is known

that the catalytic oxidation of indane gives the initial product of indane hydroperoxide, which further decomposes into indanone and indanol [26]. As shown in Scheme 2, in Step I, the catalytic reaction started with the adsorption and activation of molecular oxygen on the Au-Pd active sites, resulting in the generation of the active oxygen species, like $\bullet\text{O}^{2-}$ [30]. Then, the C–H bonds of adsorbed indane were attracted by the active oxygen species to form the intermediate indane hydroperoxide. Subsequently, the indane hydroperoxide was decomposed into indanone (Step II) and indanol (Step III) products on the surface of the Au-Pd nanocomposite. In Step IV, the obtained indanol could be further oxidized by active oxygen species to produce indanone. It can be seen in Table 2 that both indanol (38% of selectivity) and indanone (62% of selectivity) were formed when the reaction lasted for 4 h with Au-Pd/MC. Extending the reaction time to 8 h, indanol was further oxidized into indanone, and indanone selectivity was improved to 92%. Further extending the reaction time to 12 h, >99% of indanone selectivity could be obtained. This implies that the Au-Pd catalyst is not only effective for the decomposition of indane hydroperoxide into indanone and indanol but also for the dehydrogenative oxidation of indanol to indanone. Therefore, Au-Pd/MC is highly active and stable in the aerobic oxidation of indane into indanone.



Scheme 2. Proposed mechanism for the aerobic oxidation of indane in a solvent-free system using the Au-Pd/MC catalyst.

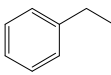
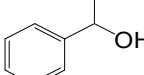
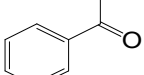
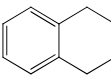
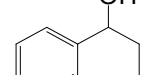
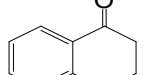
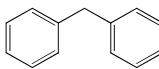
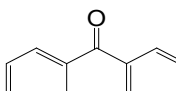
From the above analysis, several factors might contribute to the excellent catalytic activity of Au-Pd/MC. Firstly, MC support possessed a unique spherical structure with a large surface area, rich micro/mesoporosity, and oxygen-containing functional groups, providing massive anchoring sites to immobilize Au-Pd nanoparticles. Moreover, spherical carbons with a micro/mesoporous structure might serve as nanoreactors during the aerobic oxidation process, which ensures the rapid diffusion of reactants and products. The pores in the spherical carbons would provide sufficient adsorption sites and space to allow access to the transportation of reactants and products, thereby boosting catalytic efficiency. Secondly, Au-Pd/MC offered abundant acid sites, which might favor the contact between the catalyst and C–OH bond in the intermediates, thereby improving the yield of ketones. Thirdly, the Au nanocatalyst was known to have high O_2 activation ability and be effective in oxidizing various organic compounds with O_2 as the oxidant [49]. The introduction of Pd species would favor the O_2 activation to generate active oxygen species, leading to enhanced catalytic activity [30]. Overall, the cooperative effect of Au-Pd and porous carbon was responsible for the outstanding catalytic activity of Au-Pd/MC.

2.4. Solvent-Free Oxidation of Other Benzylic Compounds

The catalytic activity of the selective oxidation of various benzylic compounds was also examined to study the wider applicability of the bimetallic catalyst. The results are summarized in Table 3. Under 120 °C and 1 bar O_2 , Au-Pd/MC was capable of activating O_2 to oxidize benzylic compounds (e.g., ethylbenzene, diphenylmethane, tetralin) to form their corresponding oxidation products (Entries 1–3). Au-Pd/MC gave a low conversion of

ethylbenzene and diphenylmethane (Entry 1) but was active in the oxidation of tetralin with >50% conversion (Entry 2). The conversions would increase by prolonging the reaction time. The results confirmed that Au-Pd catalysts were active in the oxidation of C–H bonds in various benzylic compounds.

Table 3. Solvent-free oxidation of benzylic compounds catalyzed by Au-Pd/MC with 1 bar O₂.

Entry	Substrate	t (h)	Conversion (%)	Product Selectivity (%)	
1		4	11	 77	 23
2		8	52	 72	 27
3		8	12	 >99	

Reaction conditions: 4 mL substrate, 20 mg catalyst, 1 bar O₂, 120 °C.

3. Experimental Section

3.1. Chemicals

Chemicals without special descriptions were obtained from commercial companies and used without further purification. D-glucose (C₆H₁₂O₆), borax (Na₂B₄O₇), gold chloride (HAuCl₄), palladium(II) chloride (PdCl₂), sodium borohydride (NaBH₄), and indane were purchased from Sigma-Aldrich (St. Louis, MO, USA).

3.2. Preparation of Porous Carbon (MC)

A total of 9 g of D-glucose and 0.75 g of borax were dissolved in 30 mL of deionized water at room temperature. The mixture solution was transferred into a 100 mL autoclave, followed by heating at 200 °C for 8 h. The resultant solid was filtered and washed with ethanol and deionized water several times. Then, the dark brown powder can be obtained by freeze-drying. Finally, the solid precursor was post-carbonized at 550 °C for 4 h under an N₂ atmosphere. After cooling to room temperature, the black porous carbon material can be obtained, which is marked as MC.

3.3. Preparation of Metal-Supported MC Catalysts

Before use, HAuCl₄ and PdCl₂ were dissolved in a dilute HCl solution to prepare gold and palladium salt solutions, respectively. After 300 mg of as-prepared MC was dispersed in 20 mL of deionized water, a certain amount of salt solutions was sequentially added to the suspension. The total mass of Au and Pd was 3 mg, which was 1% of the carbon support. The mixture was stirred at 60 °C for 12 h and cooled to room temperature. The gold and palladium salts were reduced and loaded on MC by adding excess NaBH₄ solution (5 mL, 0.1 mol L^{−1}) drop by drop. Then, the mixture was ultrasonicated for 30 min. The precipitate was centrifuged and washed with deionized water until the ion concentration was less than 10 ppm. The resultant catalyst was dried in a vacuum drying oven at 70 °C overnight and named Au-Pd(1:3)/MC. For instance, Au-Pd/MC with an Au/Pd mass ratio of 1:3 (0.75 mg Au and 2.25 mg Pd) was named Au-Pd(1:3)/MC. Meanwhile, the other catalysts synthesized by the same method were named 1%Au/MC, Au-Pd(1:1)/MC, Au-Pd(1:2)/MC, Au-Pd(1:4)/MC, and 1%Pd/MC, depending on the different mass ratio of Au and Pd.

3.4. Characterization

Powder X-ray diffraction patterns of the samples were collected on a Bruker D8 Advance X-ray diffraction diffractometer equipped with CuK α radiation ($\lambda = 1.5147 \text{ \AA}$, Karlsruhe, Germany). N $_2$ adsorption/desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2020 instrument (Micromeritics, Norcross, GA, USA). Before the analysis, the samples were degassed at 150 °C overnight. The specific surface area of the samples was calculated by the Brunauer–Emmet–Teller (BET) method. The micropore volume was calculated by the t-plot method. The pore size distribution was determined by non-local density functional theory (DFT). The morphology of the samples was investigated using a field emission Hitachi S-4800 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan) and a transmission electron microscope (TEM, JEOL, Tokyo, Japan, JEM-2010HR) with energy-dispersive X-ray spectroscopy (EDS) analysis. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system (Kratos Analytical Ltd, Manchester, UK) with a base pressure of 10^{-9} Torr. All the binding energies were calibrated according to C 1s peak at 284.6 eV. NH $_3$ temperature-programmed desorption (TPD) was conducted on a Micromeritics Autochem 2920 chemisorption analyzer (Norcross, GA, USA).

3.5. Catalytic Experiments

In a typical reaction, 4 mL of indane and 20 mg of catalyst were added into a 10 mL three-neck glass reactor, which was fitted with a magnetic stirrer and an O $_2$ inlet tube. The reaction was carried out at a desired temperature with magnetic stirring. O $_2$ was passed into the reaction mixture and controlled by a flow meter at a constant flow rate (5 mL min $^{-1}$). After completion of the reaction, the liquid-phase solution of the reaction mixture was collected by filtration. Then, the reaction solution was diluted with acetone and measured by gas chromatography (GC, Shimadzu, Kyoto, Japan, 2010 plus). The oxidized product was confirmed by GC coupled with a mass spectrometer (GC–MS, Shimadzu, 2010 plus).

4. Conclusions

In conclusion, the bimetallic Au-Pd/MC catalysts were synthesized by a green successive borax-mediated hydrothermal carbonization of glucose, thermal pyrolysis, and chemical reduction process. The bimetallic Au-Pd nanocomposites were successfully supported on spherical porous carbon with a large surface area. The bimetallic catalysts were applied to the liquid-phase aerobic oxidation of benzylic compounds at 1 bar of O $_2$, which were effective in oxidizing indane to indanone, as well as a variety of benzylic compounds, without any additive promoters and solvents. The Au-Pd-based catalysts presented an improvement in indane conversion over their monometallic catalysts, indicating a strong synergy of Au-Pd particles. Additionally, porous carbon support also was crucial to their outstanding activity. Furthermore, the Au-Pd bimetallic catalyst kept the high activity and selectivity of ketone during five cycles. These findings are important in the design of active catalysts for the aerobic oxidation of benzylic compounds to corresponding alcohols and ketones.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal14030158/s1>, Figure S1: SEM images of the hydrochar; Figure S2: metal particle size distribution; Figure S3: XPS spectra for fresh and used Au-Pd/MC, Table S1: The quantitative chemical analysis of different samples by XPS, Table S2: The catalytic activity for the solvent-free aerobic oxidation of indane by various catalysts at 1 bar O $_2$ /air without the addition of any organic ligands or promoters. Reference [50] is cited in the supplementary materials.

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