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# One-pot solvent-free synthesis of sodium benzoate from the oxidation of benzyl alcohol over novel efficient AuAg/TiO<sub>2</sub> catalysts†

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A novel green route to synthesize sodium benzoate from the one-pot oxidation of benzyl alcohol using air as the oxidant and AuAg/TiO<sub>2</sub> as the catalyst under solvent-free conditions is presented. This process proceeds with advantages from the viewpoint of green chemistry due to non-toxic reagents, no waste emission and high recyclability of catalysts, which can retain high catalytic activity (yield > 75%) even after 6 runs.

Benzoic acid and sodium benzoate are important commodity chemicals, with wide use as a food additive, preservative, spicery, plasticizer and mordant. The commercial production of benzoic acid and sodium benzoate *via* the catalytic oxidation of toluene is achieved by heating mixture of the substrate, cobalt acetate and bromide promoter in acetic acid to 250 °C at high pressure.<sup>1</sup> Although complete conversion of toluene is obtained, the process gives rise to problems such as difficult separation of products and homogeneous catalyst, large amount of toxic waste and equipment corrosion. In addition, requirement of expensive and specialized equipment also makes the cost of production very high, along with the large amount of energy consumed by operation under extreme conditions. Therefore, more attempts are being made to find new and environmentally friendly routes, one of which is by performing the reaction under mild conditions using a variety of solid catalysts, ionic liquids or supercritical fluids.<sup>2–5</sup>

Nanosized gold has been proven to be an excellent catalyst in many reactions, including both gas- and liquid-phase oxidation,<sup>6–8</sup> the water-gas shift reaction,<sup>9</sup> hydrogenation, NO<sub>x</sub> reduction<sup>10</sup> and other processes. Among a wide range of materials, titania is recognized as one of the primary support materials from the pioneering studies on gold clusters.<sup>11–12</sup> The catalytic activity of gold is remarkably sensitive to many factors, such as the gold particle size effect,<sup>13–14</sup> the preparation method,<sup>15</sup> and the support effect.<sup>16</sup> Not only Au nanoparticle (Au NPs) catalysts are successfully applied to commercial

production, but also the research of bimetallic systems based on gold has recently shown promising potential.<sup>17</sup> Bimetallic NPs exhibit interesting electronic, optical, chemical, and biological properties due to their new bifunctional or synergistic effects.<sup>18–21</sup> The introduction of a second metal into Au NPs has been expected to enhance the catalytic activity and selectivity.<sup>22,23</sup> Silver was found especially effective to enhance catalytic activity when added to Au NPs.<sup>24–29</sup> Mou *et al.* reported that Au–Ag alloy nanoparticles supported on mesoporous aluminosilicate were applied to the low-temperature CO oxidation reaction, indicating the promising application of Au–Ag bimetallic catalysts. Herein we report the synthesis and catalytic application of AuAg/TiO<sub>2</sub> bimetallic catalyst in the manufacture of sodium benzoate from benzyl alcohol. This process was considered as an environmental-friendly, non-toxic, and energy-efficient one due to the mild reaction condition and recyclability of catalysts. Recently, Parreira *et al.* reported a similar route of selective one-pot oxidative esterification of benzyl alcohol to methyl benzoate catalyzed by modified supported gold catalysts.<sup>30</sup> However, to the best of our knowledge, no reports on the one-pot synthesis of sodium benzoate in this field can be found elsewhere.

Table 1 summarizes the BET surface area, pore volume, and average pore size of the catalysts with different Au/Ag molar ratios. The BET surface areas of the catalysts were between 30 and 50 m<sup>2</sup> g<sup>-1</sup>. The structural properties of these catalysts with various Au/Ag ratios are similar. It is also found that the loading of gold and silver determined by ICP agrees well with the nominal quantity as added.

Fig. 1 shows wide-angle XRD patterns of catalysts with different Au/Ag ratios. The diffraction pattern of the as-prepared Ag/TiO<sub>2</sub> (metallic gold, 2θ = 38.2°, 44.4° and 64.5°) of the bimetallic AuAg/TiO<sub>2</sub> catalysts are almost the same as that of Au/TiO<sub>2</sub> (metallic silver, 2θ = 38.2°, 40.67°, 44.38°, 64.66° and 77.56°). It shows that the crystalline phase of the TiO<sub>2</sub> support is the same as the as-obtained sample with the mixed anatase and rutile phase, suggesting that the preparation process has no effect on the crystalline structure of the support. The results also show that only metallic silver or gold and a small portion of AgCl was found in the as-prepared material. Yet, because silver has the same structure (fcc) and lattice constant as gold (0.409 nm *versus* 0.408 nm), they exhibit the same XRD patterns, making it difficult to distinguish gold-silver bimetallic from either monometallic phase according to

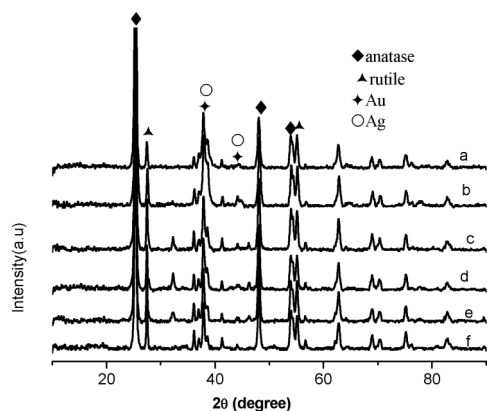
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**Table 1** Physical properties of AuAg/TiO<sub>2</sub> with different Au/Ag molar ratios

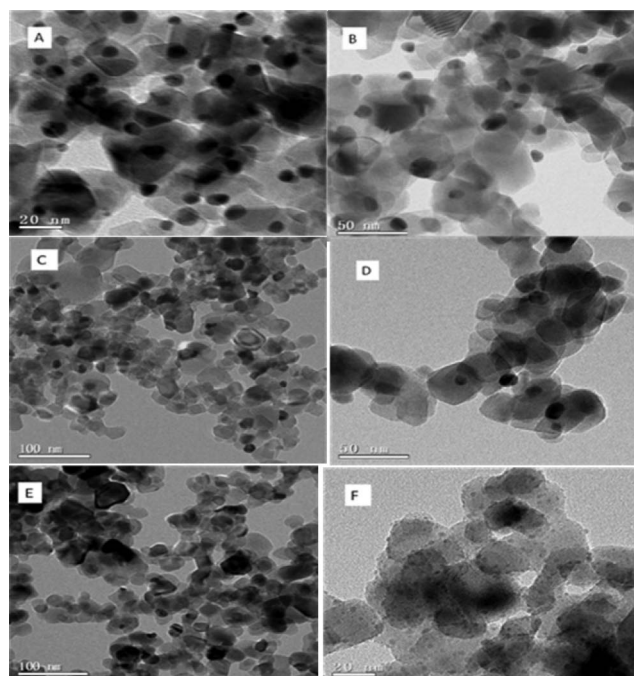
Au/Ag (nominal)	D <sub>p</sub> (nm)	D <sub>v</sub> (cm <sup>3</sup> g <sup>-1</sup> )	BET (m <sup>2</sup> g <sup>-1</sup> )	Au (wt%) <sup>a</sup>	Ag (wt%) <sup>a</sup>
4/0	36.5	0.43	49.0	7.96	0
3/1	40.0	0.44	44.6	5.94	0.96
2/2	50.9	0.42	34.2	3.99	1.82
1/3	50.0	0.42	32.8	1.98	3.01
0.5/3.5	55.5	0.43	31.2	0.98	3.58
0/4	59.2	0.47	31.9	0	3.92

<sup>a</sup> Determined by ICP

**Fig. 1** XRD patterns of AuAg/TiO<sub>2</sub> with different Au/Ag molar ratios: (a) 4/0, (b) 3/1, (c) 2/2, (d) 1/3, (e) 0.5/3.5, (f) 0/4.

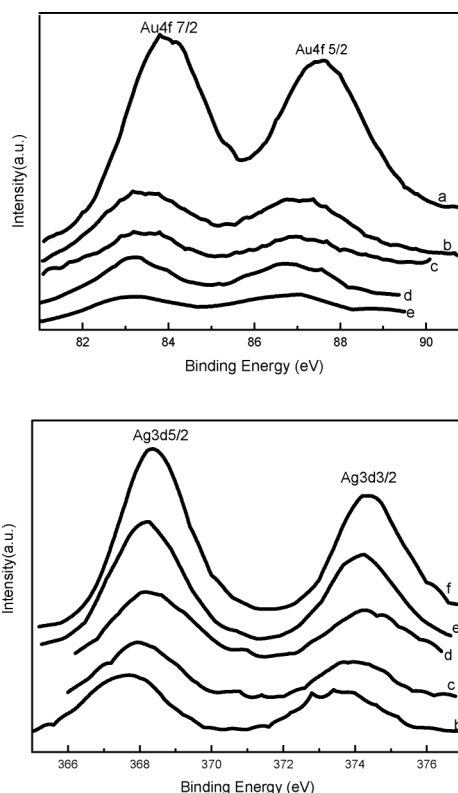
the XRD patterns.<sup>28</sup> In addition, during the preparation process of bimetallic catalyst, HAuCl<sub>4</sub> introduces Cl<sup>-</sup>, so small amount of AgCl was formed. In the XRD pattern, the reflection at 32° for catalysts c–e was ascribed to AgCl.

TEM images of AuAg/TiO<sub>2</sub> with different Au/Ag molar ratios are shown in Fig. 2. The average particle sizes of mono-

**Fig. 2** TEM images of AuAg/TiO<sub>2</sub> with different Au/Ag molar ratios: (A) 4/0; (B) 3/1; (C) 2/2; (D) 1/3; (E) 0.5/3.5; (F) 0/4.

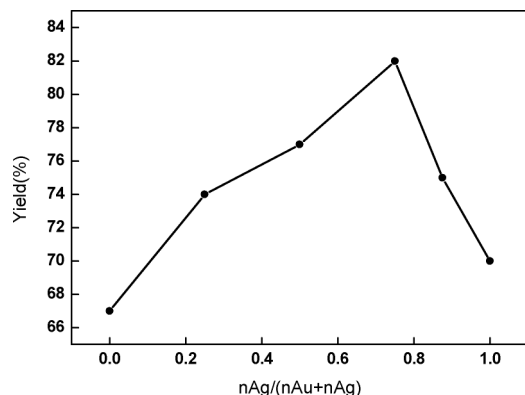
metallic catalysts, Au/TiO<sub>2</sub> and Ag/TiO<sub>2</sub>, is 6.5 and 2.6 nm, respectively. However, the particle sizes of all the bimetallic catalysts are much larger. The catalysts with Au/Ag ratios of 3/1, 2/2, 1/3 and 0.5/3.5 have average particle sizes of 9.5, 12.9, 8.7 and 10.9 nm, respectively. The nanoparticles' sizes are independent of the support surface areas. In all of the bimetallic catalysts, the average particle size of 1Au3Ag/TiO<sub>2</sub> is the smallest, which is advantageous for the catalytic activity.

Fig. 3 shows the XPS spectra of the AuAg/TiO<sub>2</sub> catalysts with different Au/Ag molar ratios. The binding energy (BE) of Au 4f<sub>7/2</sub> for monometallic catalyst Au/TiO<sub>2</sub> is 83.8 eV. And the binding energy of Au 4f<sub>7/2</sub> in bulk metallic gold is 84.0 eV. The 0.2 eV negative shift in Au 4f<sub>7/2</sub> BE between monometallic catalyst Au/TiO<sub>2</sub> and bulk metallic gold may be due to the interaction between the support and Au nanoparticles.<sup>28</sup> The binding energy of Ag 3d<sub>5/2</sub> in the Ag/TiO<sub>2</sub> was 368.4 eV, indicating that Ag is in the metallic state (368.0 eV). Moreover, for the bimetallic catalysts, Au 4f<sub>7/2</sub> BE and Ag 3d<sub>5/2</sub> BE have a

**Fig. 3** XPS spectra of AuAg/TiO<sub>2</sub> with different Au/Ag molar ratios: (a) 4/0; (b) 3/1; (c) 2/2; (d) 1/3; (e) 0.5/3.5; (f) 0/4.

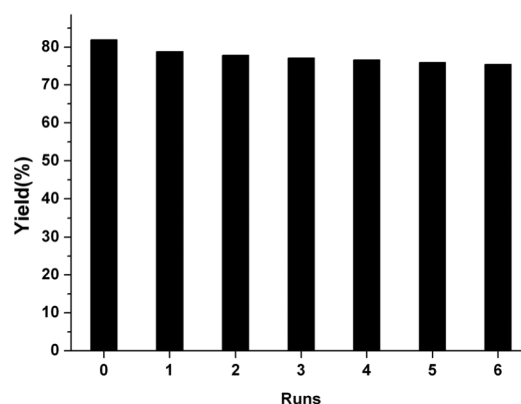
same shift direction compared with the monometallic Au/TiO<sub>2</sub> and Ag/TiO<sub>2</sub>. The negative shift of the Au 4f BE suggests that a negative charge is deposited on Au clusters, while considering the negative shift of Ag 3d BE, according to the anomalous spectral shift reported for several Ag compounds, this spectral behavior suggests that the Ag species becomes more cationic. Details can be found in Fig. S2 and S3 in the ESI.† In conclusion, these XPS results indicate that Ag donates electrons to Au sites. We assume that alloying of Ag with Au would give gold a slightly greater tendency to obtain electrons while the silver has a greater tendency to lose electrons, indicating the presence of a synergistic effect between Au and Ag.

The catalytic activity for the benzyl alcohol oxidation of the AuAg/TiO<sub>2</sub> bimetallic catalysts prepared in the present experiments with different Au/Ag ratios was investigated (Fig. 4). It is found that after 10 h there was no benzyl alcohol detected, meaning the benzyl alcohol was completely transformed. Thus, the conversions of benzyl alcohol are all 100%. The yield of bimetallic catalysts changed dramatically with the variation in Au/Ag ratios. And the catalyst with Au/Ag ratio of 1:3 had the highest yield from benzyl alcohol to sodium benzoate which reached 82%. Furthermore, all bimetallic catalysts had higher performance than monometallic ones. The Au and Ag bimetallic system shows strongly synergistic effect with better catalytic performance.



**Fig. 4** Catalytic activity test of benzyl alcohol oxidation over AuAg/TiO<sub>2</sub> with different Au/Ag molar ratios. (Reaction conditions: temperature 200 °C, reaction time 10 h, 1.08 g benzyl alcohol, 0.5 g NaOH, 0.1 g catalyst.)

Moreover, the as-prepared catalysts can be conveniently recycled with high stability. The best 1Au3Ag/TiO<sub>2</sub> bimetallic catalyst can be easily recovered and could be reused for more than six successive reactions without significant loss of the catalytic activity (Fig. 5). And the desired product with high purity and good yield can be conveniently obtained *via* simple steps: after the reaction, the mixture of solid product and catalyst were dissolved in deionized water and then the catalyst was easily recovered by centrifugation. Sodium benzoate and benzoic acid can be easily separated out by adjusting the pH of solution with diluted HCl aqueous solution from 8.0 to 2.0 spontaneously. The as-obtained white product (sodium benzoate) was obtained by simple evaporation of excess water and crystallization. While the as-obtained benzoic acid was collected by filtration, washed three times with deionized water, and dried in air.



**Fig. 5** Recyclability of 1Au3Ag/TiO<sub>2</sub> for sodium benzoate and benzoic acid synthesis. (Reaction condition: same as Fig. 4.)

In summary, we have prepared a novel efficient AuAg/TiO<sub>2</sub> bimetallic catalyst with high stability for one-pot solvent-free synthesis of sodium benzoate and benzoic acid from the green oxidation of benzyl alcohol using air as the oxidant under ambient pressure without any wastes emission. The low toxicity of titania and gold, combined with the all aqueous mild synthesis conditions made the reported synthesis route a promising one for green chemistry applications. According to our studies, the AuAg/TiO<sub>2</sub> bimetallic catalysts showed strong synergistic effect with high catalytic activity. The best-performing Au–Ag alloy catalyst was the one with a nominal Au/Ag ratio of 1:3. And even after being reused for 6 times, the 1Au3Ag/TiO<sub>2</sub> bimetallic catalyst still remained high catalytic activity (the yield >75%), which opens new possibilities for environmentally benign oxidative catalysis.

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