This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Disposed Battery Supported Ag Catalyst for Efficient Oxidation of Alcohols and Carbon Oxide

Junjie Mao, Guofeng Zhao, Dingsheng Wang* and Yadong Li

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Green-recycling of existing wastes is significant in green chemistry. Herein, we show that the disposed battery can be used as cheap and viable support to silver catalysts for gas-phase alcohol and CO oxidation. The catalyst Ag-9/MnO2 (Ag-loading: 9 wt%) is efficient for oxidizing acyclic, benzylic and polynary alcohols. For instance, Ag-9/MnO2 can oxidize cyclohexanol into cyclohexanone with 86% conversion and 88% selectivity. In addition, a special synergistic effect between Ag and Mn3O4 was revealed, which is particularly valuable to design composite catalysts. The facile strategy employed in this study can be expanded to the fabrication of other catalysts with green-reusing disposed battery as support for reactions.

Introduction
With ever-increasing serious environmental and energy issues, sustainable harvesting that begins with extracting resources from laboratory and industrial manufacturing. Typically, alcohol is oxidized in a liquid solution by using a variety of metal based homogeneous catalysts. However, these methods usually associated with low reaction rates, difficult catalyst/solvent separation, and serious toxicity issues, which hamper their wide applications. Thus, a highly selective and recyclable "green" catalyst for solvent free alcohol oxidation is required for large scale synthesis of carbonyl compounds. Moreover, the development of reusable catalysts for the gas-phase aerobic oxidation of alcohols is also valuable to the fields of organic synthesis and green chemistry.

Recently, silver nanoparticles (Ag NPs) catalysts supported on activated carbon, oxides, or polymers have been proved to be advantageous over noble metal NPs for alcohols oxidation, owing to their higher selectivity, resist leaching, and also lower catalyst cost. Moreover, it is well recognized that the selection of suitable scaffold to support Ag NPs has critical roles in determining the catalytic activity and selectivity. Thus, developing novel recycled materials supported Ag NPs for high efficient and selective alcohol oxidation could be more important.

Among various metal oxide that can support Ag NPs as catalysts, manganese oxide has been widely used as a stoichiometric oxidant for hydrocarbon or alcohol oxidation as well as support or promoter for metal or metal oxide catalysts. For example, Li et al. reported a low-temperature carbon oxide (CO) oxidation reaction by using Ag/MnO2 as a catalyst, in which MnO2 enhanced the catalytic ability of Ag NPs significantly. However, to the best of our knowledge, manganese oxide supported Ag NPs for gas-phase catalytic alcohol oxidation hasn’t been thoroughly investigated.

Here, we developed a novel catalyst using disposed battery to support Ag NPs. The in-situ reduction allows Ag NPs evenly dispersed on the MnO2 support. The as-prepared Ag/MnO2 catalyst (transformation from Ag/MnO2, using weight hourly space velocity (WHSV) = 20 h⁻¹ and molar ratio of O2 to alcoholic hydroxyl (O2/ol) = 0.6 at 280 °C) is efficient to catalyze diversified alcohols to corresponding carbonyl compounds under solvent-free conditions. As for cyclohexanol, the catalyst Ag-9/MnO2 (Ag-loading: 9 wt%) delivered a high conversion of 86% and cyclohexanone selectivity of 88% at the temperature of 280 °C. Moreover, the results based on the contrastive catalysts and characterization indicates that the formation of Ag-support interface and their interactions therein contribute to the high activity for alcohols and CO oxidation.

Results and Discussion
The original powder (MnOx) mixture from disposed battery was firstly characterized by using XRD (Figure S1). The XRD patterns of MnOx indicated the presence of manganese oxide, zinc hydroxide, and iron compounds, which was further confirmed by ICP analysis. After the purification of MnOx, pure MnO2 was successfully obtained (JCPDS 24-0735). Moreover, other crystallized impurities, such as zinc and iron compounds in original powder, were not observed. The structure of recycled MnO2 was characterized by TEM (Figure S2).
Many efforts have been devoted to conversion of cyclohexanol to surface area of MnO2 to 35.53 m2/g. The relative efficient alcohol oxidation using Ag-based catalysts synthesis of caprolactam for nylon 6 and adipic acid, widely used have been investigated. Therefore, an initial experiment been developed for alcohol oxidation. Therefore, an initial experiment was carried out over the catalyst Ag/ZrO2, and cyclohexanol conversion is 53% with a high WHSV of 20 h⁻¹ at 280 °C (Entry 3 in Table 1), but with selectivity of 62%, which restricted the manufacturing of high pure cyclohexaone by using this catalyst. The relative efficient alcohol oxidation using Ag-based catalysts prompted us to develop new systems to further enhance the catalytic performance of alcohol oxidation. Manganese oxide has superior ability to activate and supply oxygen, and has also been extensively investigated as an excellent support. A series of different silver loading MnO2 catalyst were synthesized, and then employed for the alcohols oxidation.

Cyclohexane is an important raw chemical for the organic synthesis of caprolactam from nylon 6 and adipic acid, widely used in leather industry, degreasing agents, and as detergents. Many efforts have been devoted to conversion of cyclohexanol to cyclohexanone in liquid phase. However, gas-phase oxidation as a promising route for the further industrial application has less been investigated. Here, the selective gas-phase oxidation of cyclohexanol was thoroughly investigated over the catalyst Ag/MnO2.
Ag/MnO₂ was transformed into Ag/Mn₃O₄ (Figure 1B). Fig. 3A and B show the cyclohexanol conversion and cyclohexanone selectivity over the pre-activated Ag/Mn₃O₄ catalyst. Firstly, the pre-activated Ag/Mn₃O₄ catalysts with various Ag loading were examined directly in the oxidation of cyclohexanol at 280 °C using a WHSV of 20 h⁻¹ and O₂/ol of 0.6, with the results as shown in Fig. 3. Ag-loading has strong influence on the catalytic performance. Increasing the Ag-loading from 0 to 7 wt% significantly promoted the conversion from 42 to 82% and selectivity from 45% to 77%. However, continuously increasing the Ag-loading to 11 wt% made both slightly decrease of the conversion and selectivity, maybe due to the increase size of the Ag NPs. Among all the pre-activated catalysts, the most active one was the pre-activated Ag-9/MnO₂, the conversion over Ag-9/Mn₃O₄ was further increased to 86% with selectivity of 88%. The detectable byproducts included cyclohexene, cyclohexane, benzene and small amount of COₓ. These catalytic results clearly revealed that the cyclohexanol conversion and cyclohexanone selectivity over Ag-9/Mn₃O₄ catalyst is about two times higher than that of Mn₃O₄ at the same temperature, definitely indicating Ag embedment modification of Mn₃O₄ remarkably enhanced the low-temperature activity. It should be pointed out that, unless otherwise specified, the reaction results reported in posterior parts are all based on the pre-activated catalysts. More interestingly, if raw materials from waste battery were simply washed just by drinking water, satisfactory catalytic performance can also be obtained, with conversion of 82% and selectivity of 83% at 280 °C, thus greatly increasing the potential for industrial applications and other fields.

Table 1 Oxidation of cyclohexanol over the pre-activated various catalysts. Calcination temperature: 400 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>TReaction (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ag-9/Al₂O₃</td>
<td>280</td>
<td>27</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>Ag-9/ZnO</td>
<td>280</td>
<td>45</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>Ag-9/ZrO₂</td>
<td>280</td>
<td>53</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>Ag-9/SiO₂</td>
<td>280</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>Ag-9/TiO₂</td>
<td>280</td>
<td>58</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>Ag-9/Fe₂O₃</td>
<td>280</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>Ag-9/Mn₃O₄</td>
<td>280</td>
<td>86</td>
<td>88</td>
</tr>
</tbody>
</table>

A key factor that must be considered for heterogeneous catalysts is the possibility of the active components vaporizing during the reaction, thereby leading to catalyst deactivation or, in the worst case, to the formation of an active gas-phase homogeneous catalyst. The reactor below the catalyst bed was washed by strong acid composing of HCl and HNO₃ (HCl:HNO₃ of 3:1 (vol:vol)). The ICP results of the obtained organic-product and the acid-washing liquid solution showed the absence of Ag and Mn element, indicating the thermal stability of the Ag-9/Mn₃O₄ catalyst for the alcohol oxidation. In addition, many reported results showed that the support effect plays an important, sometimes a crucial role in determining the catalyst performance. In order to investigate the support effect on catalytic performance, we prepared a series of contrastive catalysts supported on several other supports, including ZrO₂, ZnO, Al₂O₃, SiO₂, TiO₂ and Fe₂O₃. All the catalysts were evaluated by cyclohexanol with the results listed in Table 1. Generally, most catalysts demonstrated much lower cyclohexanol conversion, indicating that the Mn₃O₄ is an effective support of silver catalyst for cyclohexanol oxidation.

The reaction conditions such as reaction temperature, WHSV on the performance of Ag-9/Mn₃O₄ catalyst for the gas-phase selective oxidation of cyclohexanol were elaborate investigated, with the results as shown in Fig. 3 and Fig. S5. As shown in Fig. 3A and B, the as-obtained Mn₃O₄ and pre-activated Ag-9/Mn₃O₄ catalyst provided quite different conversion evolution behavior along with the reaction temperature. When directly testing the Mn₃O₄ in the gas-phase oxidation of cyclohexanol with increasing temperature from 240 °C to 320 °C, a low increase of cyclohexanol conversion was accompanied by obviously reduction of selectivity to target products from 78% to 30%. When silver NPs were supported on the MnO₂ to form Ag-9/Mn₃O₄ catalyst, with the increase of reaction temperature from 240 °C to 320 °C, the conversion increased from 76% to 92% while the selectivity decreased slightly to 75%.

In particular, a high selectivity to cyclohexanone with a conversion of 86% is obtained by Ag-9/Mn₃O₄ catalysts at 280 °C. However, pure Mn₃O₄ showed very poor activity for this reaction under the same conditions (conversion: ~42%, selectivity: ~45%, main by-product cyclohexene). At 280 °C, with the increase of WHSV from 5 to 20 h⁻¹, the conversion of cyclohexanol was decreased from 92% to 86% under O₂/ol of 0.6 (Fig. S5). Further increasing the WHSV from 20 to 30 h⁻¹, the cyclohexanone conversion was sharp decreased to 50% and the selectivity was almost unchanged, which indicated that the resistance time was not enough for more reactant and product molecules to react with O₂ thereby leading to the decrease of conversion. Considering a balance between high product yield and low temperature, the optimal operation parameters are WHSV of 20 h⁻¹, with O₂/ol of 0.6 at 280 °C.

Table S1 compiled the catalytic results over the pre-activated Ag-9/Mn₃O₄ for the oxidation of a range of structurally different alcohols (such as straight-chain, benzylc and polynary alcohols). The experimental results showed that the catalysis process was influenced by the structure of alcohol substrates. It is apparent that the Ag-9/Mn₃O₄ catalyst showed a higher activity for aromatic alcohols than for aliphatic ones. The pre-activated Ag-9/Mn₃O₄ could selectively oxidize 1-phenylethanol to acetophenone at the high conversion of 95% at 250 °C but only converted 23% 2-phenylethanol even at higher temperature of 280 °C. This difference may be due to the specific interactions of this substrate with the active site. In the oxidation of 1-octanol and 2-octanol, the primary linear aliphatic alcohol (1-ol) at the conversion of 40% was obtained at 270 °C with 87% selectivity to caprylic aldehyde, which has almost the same performance with the secondary counterparts (2-ol) during the oxidation. As to benzyl alcohol oxidation, selective oxidation of benzyl alcohol to benzaldehyde as one of the most important organic transformations, has attracted enormous interest due to their wide applications in the perfumery and food industries. The catalytic results indicated that Ag-9/Mn₃O₄ catalyst were very reactive among the aliphatic alcohols. Benzyl alcohol was
selectively oxidized to benzaldehyde at the conversion of 92% and the selectivity of 98% at 230 °C, which was just 25 °C higher than the boiling point of benzyl alcohol (205 °C). Furthermore, 1,2-propanediol containing two hydroxyl groups, also could be oxidized to the target product with the selectivity of 74% at the conversion of 54% at 270 °C.

Considerable attention has been paid to CO oxidation over the past years because of its great significance in the treatment of exhaust gas from automobiles and for fuel cell applications. Recently research has focused on precious metals (such as Pt, Au, and Pd), which have high activity and stability for the oxidation of CO. Nevertheless, the high cost and limited availability of the noble metals greatly hamper the practical applications and thus activate extensive interests in development of novel materials prepared with inexpensive and more abundant materials but with the excellent activity for CO oxidation.

Catalytic activity testing of CO oxidation was carried out on the as-obtained MnO₂, Ag-9/MnOx and Ag-9/MnO₂ catalysts. Clearly, we can see that Ag-9/MnOx and Ag-9/MnO₂ were more active than the recycled MnO₂. The CO conversion reached 80% at 106 °C on Ag-9/MnO₂, at 159 °C on Ag-MnOₓ and at 184 °C on recycled-MnO₂, which showed that the presence of Ag greatly improved the catalytic activity for CO oxidation. It is noteworthy that, for Ag-9/MnOₓ and Ag/MnOₓ catalysts, the temperatures of almost 100% CO conversion are 150 °C and 180 °C respectively. While for MnO₂ catalyst, the temperature of maximum CO conversion was 240 °C. Our results indicated that introducing Ag to MnO₂ would produce an efficient catalyst for CO oxidation.

From the fact that cyclohexanol conversion is very different from that, for Ag-9/MnO₂ and Ag-MnOₓ catalysts, the temperatures of maximum CO conversion were almost 100% CO conversion are 150 °C and 180 °C respectively. While for MnO₂ catalyst, the temperature of maximum CO conversion was 240 °C. Our results indicated that introducing Ag to MnO₂ would produce an efficient catalyst for CO oxidation.

Conclusions

In summary, the disposed battery supported silver catalyst was successfully synthesized which showed a high catalytic performance for the gas-phase oxidation of various alcohols and CO. For cyclohexanol oxidation, Ag-9/MnO₂ delivered a high conversion of 86% with cyclohexanone selectivity of 88% at 280 °C. Its high catalytic performance in oxidation of alcohols is attributed to the synergistic effects between Ag NPs and MnO₂ support, while Ag-MnO₂ synergistic effect is critical for carbon dioxide. This study provides an example of green-reusing the disposed battery for alcohols and CO oxidation. Further investigations of the industrial application of this catalyst to other oxidation processes as well as the precise mechanism of this oxidation process are currently in progress.

Acknowledgments

Fig. 4 Conversion-temperature curves for CO oxidation over MnO₂, Ag-9/MnOₓ and Ag-9/MnO₂ catalysts.

Fig. 5 (A) Mn 2p XPS spectra of (a) Ag-9/MnO₂ (b) Ag-9/MnOₓ and (c) MnO₂. (B) Ag 3d XPS spectra of (a) Ag-9/MnO₂ (b) Ag-9/MnOₓ and (c) Ag NPs. (C) HRTEM image of Ag-9/MnO₂ catalyst. (D) HRTEM image of the region indicated with a box in panel D.
This work was supported by the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (2011CB932401, 2011CB930050, 2012CB212402), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (201321), Specialized Research Fund for the Doctoral Program of Higher Education (201300212003), and the National Natural Science Foundation of China (21221062, 21131004, 21303933, 21322107).

Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China; E-mail: wangdingsheng@tsinghua.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental details, XRD, TEM, N2 adsorption–desorption isotherms and pore size distribution curves of samples; Oxidation of various alcohols over the catalysts. See DOI: 10.1039/b000000x/

References

The disposed battery supported silver catalyst was successfully synthesized which showed high catalytic performance for oxidation of alcohols and CO.