RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSC Advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

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/Mn_3O_4 (Ag-loading: 9 wt%) is efficient for oxidizing acyclic, benzylic and polynary alcohols. For instance, Ag-9/Mn_3O_4 can oxidize cyclohexanol into cyclohexanone with 86% conversion and 88% selectivity. In addition, a special synergistic effect between Ag and Mn_3O_4 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 earth using cost-effective techniques which minimize negative impacts is becoming more and more important.[1] Taking battery recycle as an example, global per capital, per annum battery consumption of 330 g can leaves a massive residue of untreated battery waste, which not only pollutes the environment but also leads to great energy waste.[2,3] Thus, establishing battery-recycle-system is of significance to sustainable development.

The selective oxidation of alcohols to corresponding carbonyl compounds is of interest due to its fundamental importance for laboratory and industrial manufacturing.[4-8] Traditionally, 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 oxidization is required for large scale synthesis of carbonyl compounds.[9,10] 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 oxidization, owing to their higher selectivity, resist leaching, and also lower cost.[11,12] 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 oxidization 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 oxidization as well as support or promoter for metal or metal oxide catalysts.[13-15] For example, Li et al. reported a low-temperature carbon oxide (CO) oxidation reaction by using Ag/MnO_2 as a catalyst, [16] in which MnO_2 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 MnO_2 support. The as-prepared Ag/Mn_3O_4 catalyst (transformation from Ag/MnO_2, using weight hourly space velocity (WHSV) = 20 h^{-1} and molar ratio of O_2 to alcoholic hydroxyl (O_2/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/Mn_3O_4 (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 (MnO_x) mixture from disposed battery was firstly characterized by using XRD (Figure S1). The XRD patterns of MnO_x indicated the presence of manganese oxide, zinc hydroxide, and iron compounds, which was further confirmed by ICP analysis. After the purification of MnO_x , pure MnO_2 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 MnO_2 was characterized by TEM (Figure S2).

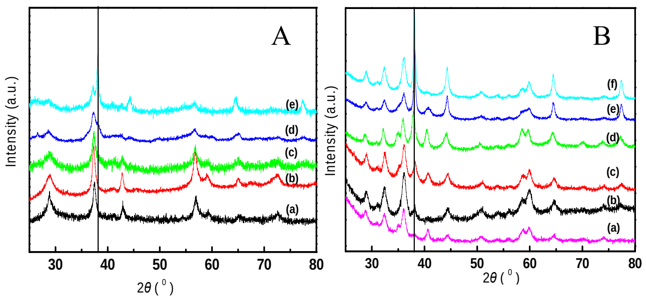


Fig. 1 (A) XRD patterns of the before pre-activation treatment for samples: (a) Ag-3/MnO_2, (b) Ag-5/MnO_2 (c) Ag-7/MnO_2 (d) Ag-9/MnO_2 (e) Ag-11/MnO_2 ; (B) XRD patterns of the Pre-activation catalysts: (a) Mn_3O_4, (b) Ag-3/Mn_3O_4, (c) Ag-5/Mn_3O_4, (d) Ag-7/Mn_3O_4, (e) Ag-9/Mn_3O_4, (f) Ag-11/Mn_3O_4; Pre-activation conditions: catalysts for the gas-phase oxidation of cyclohexanol was pre-activation, using WHSV = 20 h^{-1} and O_2/ol = 0.6 at 280 °C in advance.

Figure 1A showed the XRD patterns of Ag/MnO_2, and the results showed that the MnO_2 phase was kept unchanged after Ag deposition. Moreover, metallic silver diffraction peaks were not observed over the catalysts with low Ag-loading (3%-5%), but then appeared over the catalysts with high Ag-loading from 7% to 11%. Then, the catalysts Ag/MnO_2 were characterized by TEM (Figure S3), and the Ag NPs were highly dispersed on the surface of MnO_2 support. Taking the catalyst Ag-9/MnO_2 as an example, the Ag particle size is between 6-8 nm according to the PSD histogram with the mean size of 6.99 nm (Figure 2A inset). The d-spacing for adjacent lattice fringes measured from several different regions was 2.36 Å (Figure 2B), which is close to that of the (111) planes of a face-centered cubic (fcc) Ag crystal. The high-angle annular dark-field scanning TEM (HAADF-STEM) image (Fig. 2C) further confirmed Ag NPs are well-dispersed on MnO_2 surface. The energy-dispersive X-ray spectroscopy (EDS) mapping profile (Fig. 2D) further manifested the homogeneous distribution of Ag, Mn, and O in Ag-9/MnO_2 nanocrystals. The above results indicated that the employed in-situ reduction method is simple and facile to fabricate the Ag/MnO_2 catalyst. N_2 adsorption-desorption isotherms (Figure S4) indicated the mesoporous structure of all the samples, with the Barrett-Joyner-Halenda (BJH) pore size of 12.88 nm for MnOx, 32.60 nm for MnO_2, and 21.67 nm for Ag-9/MnO_2 (Fig. S4, insets). BET measurements indicated that MnO_x and MnO_2 have a BET surface area of 22.98 m^2/g, 41.56 m^2/g, respectively, while the deposition of Ag NPs onto MnO_2 surface slightly reduced the surface area of MnO_2 to 35.53 m^2/g.

Cyclohexanone is an important raw chemical for the organic synthesis of caprolactam fornylon 6 and adipic acid, widely used in leather industry, degreasing agents, and as detergents.[17,18] Many efforts have been devoted to conversion of cyclohexanol to cyclohexanone in liquid phase.[19,20] However, gas-phase oxidation as a promising route for the further industrial application has less been investigated.[21] Here, the selective gas-phase oxidation of cyclohexanol was thoroughly investigated over the catalyst Ag/Mn_3O_4.

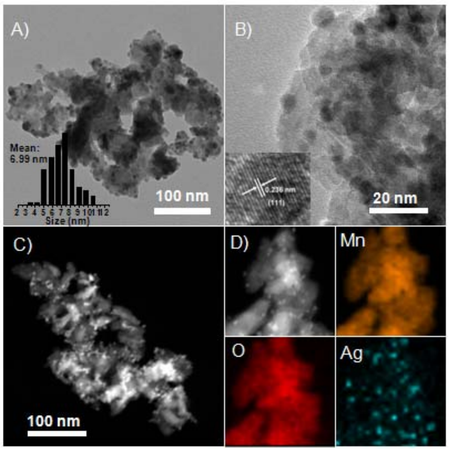


Fig. 2 (A) TEM images of Ag-9/MnO_2 (Inset is the Ag particle size distribution), (B) HRTEM images of Ag-9/MnO_2 (Inset is the enlarged HRTEM image of Ag nanocrystals), (C) HAADF-STEM images of Ag-9/MnO_2 nanocrystals, (D) HAADF-STEM image together with the EDX mapping of Ag-9/MnO_2 nanocrystals.

In recent years, silver based heterogeneous catalysts have been developed for alcohol oxidation. Therefore, an initial experiment was carried out over the catalyst Ag/ZrO_2, 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 MnO_2 catalyst were synthesized, and then employed for the alcohols oxidation.

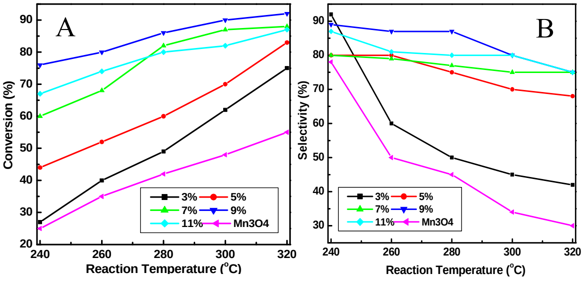


Fig. 3 Catalytic performance of the catalysts with various Ag loading. (A) cyclohexanol conversion and (B) cyclohexanone selectivity over the pre-activated Ag/Mn_3O_4 catalyst. (The gas-phase oxidation of cyclohexanol was performed using O_2/ol of 0.6 and WHSV of 20 h^{-1}. Catalyst: 0.1 g; Quartz sands: 0.2 g (100-150 mesh))

We first studied the efficiency of MnO_2-supported silver catalysts with varying silver loading for solvent-free alcohol oxidation by molecular oxygen. Of especially emphasis is an observation that the catalytic activity of the Ag/MnO_2 catalysts for the gas-phase oxidation of cyclohexanol was enhanced after pre-activation using WHSV = 20 h^{-1} and O_2/ol = 0.6 at 280 °C in advance. The XRD results indicated that after pre-activation,

Ag/MnO_2 was transformed into Ag/Mn_3O_4 (Figure 1B). Fig. 3A and B show the cyclohexanol conversion and cyclohexanone selectivity over the pre-activated Ag/Mn_3O_4 catalyst. Firstly, the pre-activated Ag/Mn_3O_4 catalysts with various Ag loading were examined directly in the oxidation of cyclohexanol at 280 ^oC using a WHSV of 20 h^{-1} and O_2/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/Mn_3O_4, the conversion over Ag-9/Mn_3O_4 was further increased to 86% with selectivity of 88%. The detectable byproducts included cyclohexene, cyclohexane, benzene and small amount of CO_x. These catalytic results clearly revealed that the cyclohexanol conversion and cyclohexanone selectivity over Ag-9/Mn_3O_4 catalyst is about two times higher than that of Mn_3O_4 at the same temperature, definitely indicating Ag embedment modification of Mn_3O_4 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 ^oC, 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 ^oC.

Entry	Catalysts	$T_{Reaction}$ (^oC)	Conversion (%)	Selectivity (%)
1	Ag-9/Al_2O_3	280	27	74
2	Ag-9/ZnO	280	45	58
3	Ag-9/ZrO_2	280	53	62
4	Ag-9/SiO_2	280	22	23
5	Ag-9/TiO_2	280	58	52
6	Ag-9/Fe_2O_3	280	75	60
7	Ag-9/Mn_3O_4	280	86	88

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 HNO_3 (HCl:HNO_3 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/Mn_3O_4 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 ZrO_2, ZnO, Al_2O_3, SiO_2 TiO_2 and Fe_2O_3. 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 Mn_3O_4 is an effective support of silver catalyst for cyclohexanol oxidation.

The reaction conditions such as reaction temperature, WHSV on the performance of Ag-9/Mn_3O_4 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 Mn_3O_4 and pre-activated Ag-9/Mn_3O_4 catalyst provided quite different conversion evolution behavior along with the reaction temperature. When directly testing the Mn_3O_4 in the gas-phase oxidation of cyclohexanol with increasing temperature from 240 ^oC to 320 ^oC, 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 MnO_2 to form Ag-9/Mn_3O_4 catalyst, with the increase of reaction temperature from 240 ^oC to 320 ^oC, 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/Mn_3O_4 catalysts at 280 ^oC. However, pure Mn_3O_4 showed very poor activity for this reaction under the same conditions (conversion: ~42%, selectivity: ~45%, main by-product cyclohexene). At 280 ^oC, with the increase of WHSV from 5 to 20 h^{-1}, the conversion of cyclohexanol was decreased from 92% to 86% under O_2/ol of 0.6 (Fig. S5). Further increasing the WHSV from 20 to 30 h^{-1}, the cyclohexanol 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 O_2 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 O_2/ol of 0.6 at 280 ^oC.

Table S1 compiled the catalytic results over the pre-activated Ag-9/Mn_3O_4 for the oxidation of a range of structurally different alcohols (such as straight-chain, benzylic 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/Mn_3O_4 catalyst showed a higher activity for aromatic alcohols than for aliphatic ones. The pre-activated Ag-9/Mn_3O_4 could selectively oxidize 1-phenylethanol to acetophenone at the high conversion of 95% at 250 ^oC but only converted 23% 2-phenylethanol even at higher temperature of 280 ^oC. 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 ^oC 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.[9,21-23] The catalytic results indicated that Ag-9/Mn_3O_4 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 ^oC, which was just 25 ^oC higher than the boiling point of benzyl alcohol (205 ^oC). 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 ^oC.

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.[16,24] Recently research has focused on precious metals (such as Pt, Au, and Pd), which have high activity and stability for the oxidation of CO.[25-28] 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.

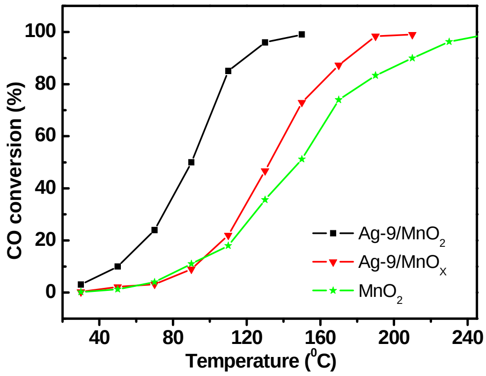


Fig. 4 Conversion-temperature curves for CO oxidation over MnO_2, Ag-9/MnO_x and Ag-9/MnO_2 catalysts.

Catalytic activity testing of CO oxidation was carried out on the as-obtained MnO_2, Ag-9/MnO_x and Ag-9/MnO_2 (Fig. 4). Clearly, we can see that Ag-9/MnO_x and Ag-9/MnO_2 were more active than the recycled MnO_2. The CO conversion reached 80% at 106 ^oC on Ag-9/MnO_2, at 159 ^oC on Ag-MnO_x and at 184 ^oC on recycled-MnO_2, which showed that the presence of Ag greatly improved the catalytic activity for CO oxidation. It is noteworthy that, for Ag-9/MnO_2 and Ag/MnO_x catalysts, the temperatures of almost 100% CO conversion are 150 ^oC and 180 ^oC respectively. While for MnO_2 catalyst, the temperature of maximum CO conversion was 240 ^oC. Our results indicated that introducing Ag to MnO_2 would produce an efficient catalyst for CO oxidation.

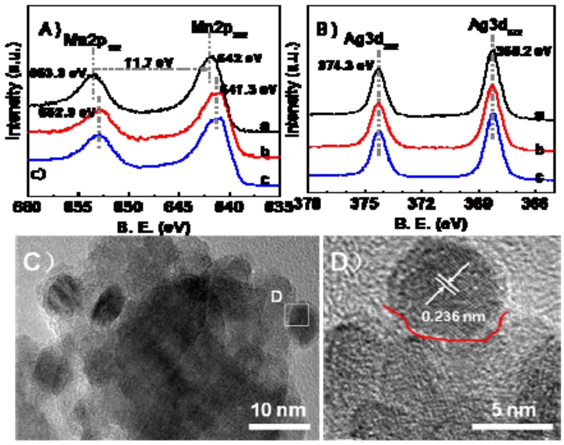


Fig. 5 (A) Mn 2p XPS spectra of (a) Ag-9/Mn_3O_4 (b) Ag-9/MnO_2 and (c) MnO_2, (B) Ag 3d XPS spectra of (a) Ag-9/Mn_3O_4 (b) Ag-9/MnO_2 and (c) Ag NPs, (C) HRTEM image of Ag-9/Mn_3O_4 catalyst. (D) HRTEM image of the region indicated with a box in panel D.

From the fact that cyclohexanol conversion is very different over the catalysts with various supports (Ag/ZrO_2, Ag/ZnO, Ag/Al_2O_3, Ag/SiO_2, Ag/TiO_2 and Ag/Fe_2O_3), it is evident the nature of the supports plays a vital role in the performance of the silver for present reaction. The XRD results have showed that MnO_2 in the fresh catalyst by pre-activation was transformed into Mn_3O_4 during the process of cyclohexanol oxidation. Similarly, XPS results showed that the surface composition of support was transformed from MnO_2 into Mn_3O_4, and Ag surface remained almost unchanged (Fig.5A and B). These results indicating the support is an active participant for the cyclohexanol oxidation. However, for the catalyst with no silver loading, the cyclohexanol conversion was only 42% at 280 ^oC accordingly. The results of control experiment showed that, for inactive supports (ZrO_2, ZnO, Al_2O_3, and SiO_2) supported Ag catalysts as well as sole MnO_x catalyst, the catalytic activity for alcohol oxidation was very low, while for Ag-9/MnO_x catalyst, the activity greatly enhanced. Similarly for the CO oxidation, Ag-9/MnO_2 showed better catalytic performance compared to the sole MnO_2 catalyst. For the Ag/oxides system, several papers were focused on the CO oxidation,[16,29] HCHO oxidation[30] and gas-phase selective oxidation of benzyl alcohol,[22] and they all proposed that the Ag-oxides interaction was crucial for the corresponding reactions therein. Based on our control experiment and reported results, it was proposed that there should exist strong metal-support interaction (SMSI) between Ag and MnO_x. In order to verify this proposal, the used Ag-9/Mn_3O_4 was visualized by HRTEM. Interestingly, the results showed clear Ag-Mn_3O_4 interface (Figure 5C and D). Other oxide-metal interfacial or perimeter sites and SMSI therein have been known for their high activity in various reactions, such as Au/oxides[31,32] and Pt/oxides.[33-35] From the above results, it is reasonable to propose that the Ag-Mn_3O_4 interface and their interactions therein play a great important or the critical role in the oxidation of alcohols and CO.

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/Mn_3O_4 delivered a high conversion of 86% with cyclohexanone selectivity of 88% at 280 ^oC. Its high catalytic performance in oxidation of alcohols is attributed to the synergistic effects between Ag NPs and Mn_3O_4 support, while Ag-MnO_2 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

This work was supported by the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (2011CB932401, 2011CBA00500, 2012CB224802), 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 (20130002120013), and the National Natural Science Foundation of China (21221062, 21131004, 21390393, 21322107).

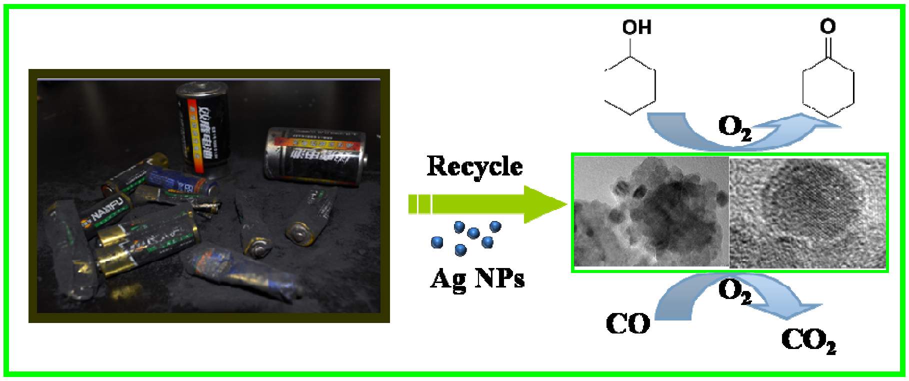
Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China; E-mail: wangdingsheng@tsinghua.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental details, XRD, TEM, N_2 adsorption–desorption isotherms and pore size distribution curves of samples; Oxidation of various alcohols over the catalysts. See DOI: 10.1039/b000000x/

References

1. A. A. White, M. S. Platz, D. M. Aruguete, S. L. Jones, L. D. Madsen and R. D. Wesson, *ACS Sustainable Chem. Eng.*, 2013, **1**, 871.
2. M. J. Smith and F. M. Gray, *J. Chem. Educ.*, 2010, **87**, 162.
3. A. J. Pedersen, F. J. Frandsen, C. Riber, T. Astrup, S. N. Thomsen, K. Lundtorp and L. F. Mortensen, *Energy Fuels*, 2009, **23**, 3475.
4. T. Mallat, Z. Bodnar, P. Hug and A. Baiker, *J. Catal.*, 1995, **153,** 131.
5. A. Corma and H. Garcia, *Chem. Soc. Rev.*, 2008, **37**, 2096.
6. D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science,* 2006, **311**, 362.
7. T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037.
8. A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180.
9. G. F. Zhao, H. Y. Hu, M. M. Deng, M. Ling and Y. Lu, *Green Chem,* 2011, **13**, 55.
10. J. J. Mao, D. S. Wang, G. F. Zhao, W. Jia and Y. D. Li, *CrystEngComm*, 2013, **15**, 4806.
11. L. H. Jia, S. Zhang, F. N. Gu, Y. Ping, X. F. Guo, Z. Y. Zhong and F. B. Su, *Micro. Meso. Mater.,* 2012, **149**, 158.
12. H. Wu, P. Wang, H. He and Y. Jin, *Nano Res.,* 2012, **5**, 135.
13. L. C. Wang, Y. M. Liu, M. Chen, Y. Cao, H. Y. He and K. N. Fan, *J. Phys. Chem. C*, 2008, **112**, 6981.
14. L. C. Wang, X. S. Huang, Q. Liu, Y. M. Liu, Y. Cao , H. Y. He, K. N. Fan and J. H. Zhuang, *J. Catal.,* 2008, **259**, 66.
15. L. C. Wang, L. He, Q. Liu, Y. M. Liu, M. Chen, Y. Cao, H. Y. He and K. N. Fan, *Appl. Catal. A: General,* 2008, **344**, 150.
16. R. Xu, X. Wang, D. S. Wang, K. B. Zhou and Y. D. Li, *J. Catal.,* 2006, **237,** 426.
17. X. Yang, L. Du, S. J. Liao, Y. X. Li, and H. Y. Song, *Catal. Commun,* 2012, **17**, 29.
18. Y. Li, X. Xu, P. F. Zhang, Y. T. Gong, H. R. Li, and Y. Wang, *RSC. Adv,* 2013, **3**, 10973.
19. P. Liu, Y. J. Guan, R. A. Santen, C. Li, and E. J. M. Hensen, *Chem. Commun,* 2011, **47**, 11540.
20. T. Wang, H. Shou, Y. Kou, and H. C. Liu, *Green Chem,* 2009,**11**,562.
21. G. F. Zhao, H. Y. Hu, M. M. Deng and Y. Lu, *Chem. Commun,* 2011, **47**, 9642.
22. M. M. Deng, G. F. Zhao, Q. S. Xue, L. Chen, and Y. Lu, *Appl. Catal. B,* 2010, **99**, 222.
23. C. D. Pina, E. Falletta, and M. Rossi, *J. Catal.,* 2008, **260**, 384.
24. S. J. Huang, K. J. Hara and A. Fukuoka, *Energy Environ. Sci.*, 2009, **2**, 1060.
25. H. Xu, Q. Fu, Y. X.Yao and X. H. Bao, *Energy Environ. Sci.*, 2012, **5**, 6313.
26. J. R. Gaudet, A. Riva, E. J. Peterson, T. Bolin and A. K. Datye, *ACS Catal.*, 2013, **3** , 846.
27. X. Zhang, H. Wang and B. Q. Xu, *J. Phys. Chem. B*, 2005, **109**, 9678.
28. J. W. Zhang, L. Zhang, Y. Y. Jia, G. X. Chen, X. Wang, Q. Kuang, Z. X. Xie and L. S. Zheng, *Nano Res.*, 2012, **5**, 618.
29. G. G. Xia, Y. G. Yin,W. S. Willis, J. Y. Wang, and S. L. Suib, *J. Catal,* 1999, **185**, 91
30. Z. W. Huang, X. Gu, Q. Q. Cao, P. P. Hu, J. M. Hao, J. H Li, and X. F. Tang, *Angew. Chem. Int. Ed,* 2012, **51**, 4198.
31. M. Haruta, *Cattech,* 2002, **6**, 102.
32. J. C. Chen, R. Y. Zhang, L. Han, B. Tu and D. Y. Zhao, *Nano Res.*, 2013, **6,** 871.
33. C. T. Campbell, *Nat. Chem.,* 2012, **4**, 597.
34. Q. Fu, W. Li, Y. Yao, H. Liu, H. Su, D. Ma, X. Gu, L. Chen, Z. Wang, H. Zhang, B. Wang and X. Bao, *Science,* 2010, **328**, 1141.
35. Q. Fu, F. Yang, and X. Bao, *Acc. Chem. Res,* 2013, **46**, 1692.

A table of contents entry



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