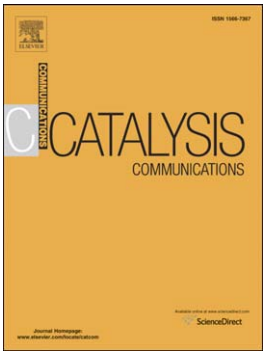

Au NPs@ polystyrene resin for mild and selective aerobic oxidation of 1,4 dioxane to 1,4 dioxan-2-ol

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Au NPs@ polystyrene resin for mild and selective aerobic oxidation of 1, 4 dioxane to 1, 4 dioxan- 2-ol

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Abstract

Supported gold nanoparticles of sizes 5-8 nm have emerged as highly efficient catalyst for the oxidation of 1, 4 dioxane a saturated ether using elemental oxygen at low temperature. GC-MS analysis of the reaction mixture showed > 85 % conversion of 1, 4 dioxane with a TON of 1120 h^{-1} to 1, 4 dioxan-2-ol with 90 % selectivity. 1, 4 dioxan-2- one was obtained as the major byproduct along with traces of acetic acid and methoxy dioxalane. The catalyst displayed excellent stability and recyclability. TEM analysis of reused catalyst indicated that there was no significant change in the size, shape and morphology of gold nanoparticles.

Keywords: resin supported AuNPs, oxidation of 1, 4 dioxane, molecular oxygen, heterogeneous catalyst

Introduction

Usage of nanoparticles as catalysts has revolutionized the field of chemical oxidation in the past two decades. Especially noteworthy is the catalysis by supported gold nanoparticles (AuNP). which has turned out to be selective, clean and with remarkable recyclability. In fact AuNP catalysed oxidation reactions have become one of the most fertile fields of research owing to its capability to chemisorb and dissociate molecular oxygen at low temperatures [1-5]. Most of the initial research in this field was limited to AuNPs supported on metal oxides such as TiO_2, CeO_2 and Fe_2O_3 for the oxidation of CO in air [6-10]. But gradually, oxidation of a variety of substrates other than CO such as aldehyde [11], cyclohexene [12-13], alcohols [14-15], glucose [16] etc. were also reported.

1, 4 dioxane is an important chemical that is widely used as solvent for the synthesis of dyes, oils, paints, organic molecules, pesticides, plastics etc. It is a probable carcinogen and is classified as hazardous compound [17]. It belongs to a class of saturated cyclic ethers that are part of numerous natural products and associated with bioactivity [18]. Not much work has been reported in literature about its oxidation. Owing to its probable carcinogenicity, a few studies on its degradation by photocatalytic [19-20] and biological processes [21-22] have been performed and reported. There are also few reports of its heterogeneous catalytic oxidation using Fe [23], Pt [24] and Ti [25] as catalysts on porous inorganic supports. In case of iron the activity of catalyst was studied at high temperature leading to complete oxidation of dioxane to CO [23] and in case of Ti catalyzed oxidation, H_2O_2 was used as oxidant [25].

To the best of our knowledge, there are no reports on the thermal oxidation of 1, 4 dioxane catalyzed by gold nanoparticles. With circumstantial, and in continuation of our endeavours towards supported nanocatalysis, we herein report the Au NPs@resin catalyzed selective oxidation of 1,4 dioxane to 1,4 dioxan-2-ol using molecular oxygen as green

oxidant. We studied the effect of various reaction parameters such as temperature, nature of the oxidant (H_2O_2, TBHP, and O_2), catalyst quantity, reusability, reaction time etc. to optimize conditions for the best yield of 1,4 dioxan-2-ol..

2. Experimental and Instrumentation

2.1 Materials

$HAuCl_4$ were purchased from Sigma Aldrich. Amberlite XAD-4 resin was purchased from Fluka Chemical Corporation. 1,4 dioxane used was of analytical grade. $NaBH_4$ and all other solvents were purchased from Finar chemicals. The peroxides, H_2O_2 (30 % in water) and TBHP (70 % in water), were purchased from Spectrochem Fine Chemicals Ltd. All glassware was systematically cleaned with aquaregia. Cross linked polystyrene resin Amberlite XAD-4 was impregnated with gold nanoparticles by a method reported earlier in our lab. The average concentration of impregnated gold is 0.630 mg/g of the resin [26].

2.2 Instrumentation

GC–MS measurements were carried on Perkin Elmer USA Auto system XL; carrier gas Helium, Column PE–5MS (condition: injection temperature 200 °C, column flow 0.7 mL / min, carrier gas helium, oven temp varied from 70 to 280 °C at 10 °C per min. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out on a HJY Ultima-2 instrument: 1000 W, nebulizer pressure 2.96, nebulizer flow 1.29, wave length 242.795 nm. High resolution transmission electron microscopy (HRTEM) pictures were taken using a Hitachi (H-7500) instrument attached with EDX as per protocol mentioned in ref. 26.

2.3 Catalytic oxidation of 1, 4 dioxane using O_2

In a typical experiment, oxidation of styrene with O_2 was performed in a 25 mL two-necked round bottom flask equipped with a reflux condenser and filled with 10 mmol of 1, 4 dioxane, and 150 mg of catalyst. The reaction mixture was heated at 80 ˚C under gentle stirring. At atmospheric pressure, O_2 gas from a balloon was bubbled into the reaction mixture at a certain stable flow rate controlled by a mass flow controller. Care should be taken while heating the reaction mixture as dioxane vapours can form a highly combustible mixture with pure oxygen and explosive peroxides (MSDS 1,4 dioxane). After 24 h, the catalyst was separated from the reaction mixture by simple filtration and the reaction mixture after proper dilution with methanol was analyzed using GC-MS.

2.4 Catalytic oxidation of 1, 4 dioxane using H_2O_2 and TBHP

A 25 mL round bottom flask equipped with reflux condenser, was filled with 1, 4 dioxane (10 mmol), 4 ml oxidant (H_2O_2 or TBHP), and 150 mg catalyst. The flask was placed in an oil bath and the reaction mixture was heated at 80 ˚C with gentle stirring. After 24 h, the catalyst was separated by filtration and the reaction mixture was extracted in ethyl acetate. The extracted organic layer was dried with anhydrous Na_2SO_4 and the product was subjected to GC-MS analysis.

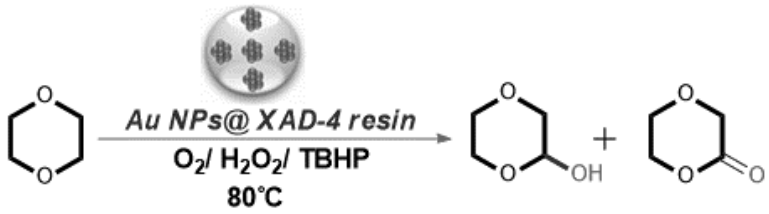
3. Result and Discussion

We have earlier reported the synthesis of gold nanoparticles supported on XAD-4 resin beads (see ESI), which were found to be highly efficient, stable and reusable catalysts [26]. In a nonfunctional resin like XAD-4, the existent micro-pores are responsible for the stabilization of gold nanoparticles by virtue of steric hindrance afforded by polymer network along with the electrostatic forces between the resin matrix and the nanoparticles. In the absence of any strong surface interactions these nanoparticles are highly active. During our studies on AuNPs catalyzed oxidation reactions we discovered that the catalyst is active

towards oxidation of 1, 4 dioxane which was being used as solvent in the reaction and we decided to study it in detail.

3.1 Oxidation of 1, 4 dioxane

A systematic investigation of the catalytic activity of the AuNPs@ XAD-4 toward the oxidation of 1, 4 dioxane was carried out in presence of molecular O_2 at ambient pressure, H_2O_2 and tert-butyl hydroperoxide (TBHP). GC-MS analysis of the reaction mixture indicated a high conversion of 1, 4 dioxane (85 %) in molecular oxygen as compared to other oxidants. (Scheme 1). Conversion of 1, 4 dioxane in the presence of different oxidants was carried out and the results are shown in Table 1. It was also observed that 1, 4 dioxan-2-ol (90 %) was the major product while 1, 4 dioxan-2-one was obtained as major side product along with trace amount of acetic acid and methoxy dioxalane (Entry 3). The products as identified by GC-MS showed retention time of 2.10, 3.40 and 5.20 min respectively for 1, 4 dioxane, 1, 4 dioxane 2-ol and 1, 4 dioxan-2-one (see ESI). 1, 4 dioxan-2-ol was identified by its characteristic m/z peaks at 104, 103, 102, 73, 58, 44, 42 (see ESI) whereas, 1, 4 dioxan-2-one was identified by its characteristic m/z peaks at 103, 102, 73, 58, 44, 42 (see ESI). Oxidation of C-H bond of 1, 4 dioxane, a saturated ether is an indication of the highly active nature of AuNPs supported on the resin.



Scheme 1. Reaction scheme for the oxidation of 1, 4 Dioxane by Au NPs@ Resin.

Table 1. Effect of oxidant on oxidation of 1, 4 dioxane by Au NPs@ Resin.

		Selectivity		
Oxidant	Conversion (%)	1, 4 dioxan-2-ol	1, 4 dioxan-2-one	Other
TBHP*	25	14	47	39
H_2O_2*	40	35	55	10

O_2	85	90	07	03

Reaction conditions: 1, 4 dioxane (10 mmol), catalyst (150 mg), 24 hour; 80 ° C * H_2O_2 or TBHP (4 mL) conversion and selectivity determined by GC-MS analysis.

3.3 Effect of Temperature

Effect of temperature on conversion of the reactant was studied at temperatures ranging from 60 to 100 ˚C and it was observed that at 60 ˚C the conversion of 1, 4 dioxane was 36 % with 56 % selectivity for 1, 4 dioxan-2-ol. As we increased the temperature from 60 ˚C to 80 ˚C, the conversion increased from 36 to 85 %. At this temperature maximum selectivity for 1, 4 dioxan-2-ol (90 %) was observed. On further raising the temperature from 80 to 100 ˚C, it was observed that conversion of 1, 4 dioxane increased from 85 to 92 % but selectivity for 1, 4 dioxan-2-ol decreased to 40 % due to its over oxidation (Figure 1). Therefore, 80 ˚C was selected as the optimum temperature and the effect of other important parameters such as catalyst concentration and reaction time were studied at this temperature.

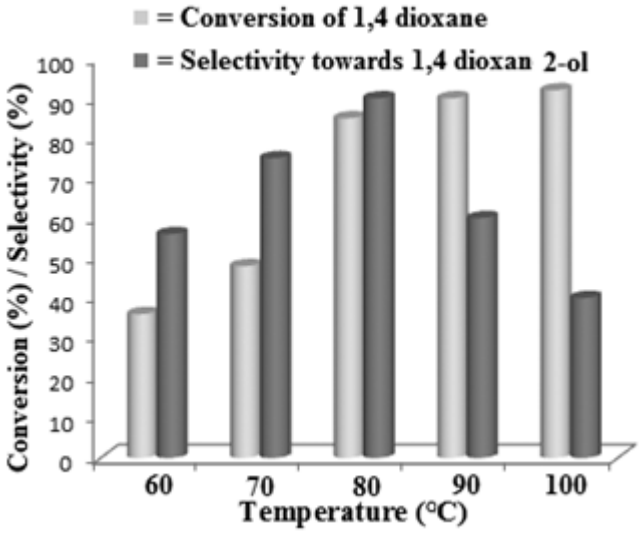


Figure 1. Effect of Temperature on 1, 4 dioxane oxidation. (Reaction conditions: 1, 4 dioxane (10 mmol), Catalyst (150 mg), 24 h, 1 atm O_2).

3.4 Effect of reaction time

To ascertain the conversion of 1, 4 dioxane and selectivity of 1, 4 dioxane 2-ol, reaction mixture was analyzed at intervals of 4 h by GC-MS. It was observed that after 4 h, the conversion of 1, 4 dioxan-2-ol was only 28 % with 70 % selectivity for 1, 4 dioxan-2-ol as shown in the Figure 2. As the time increased from 4 h to 24 h, conversion of 1, 4 dioxane increased from 28 to 85 %. Further increase in the reaction time up to 28 h increased the conversion of 1,4 dioxane from 85 to 90 % but selectivity decreased to 65 %.

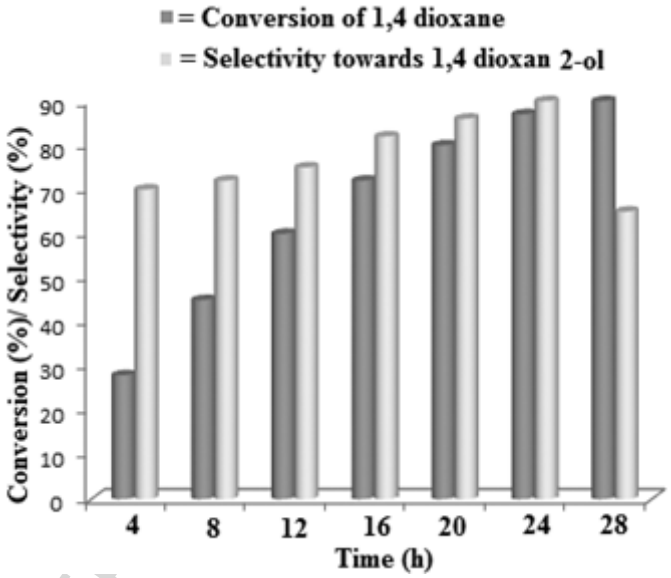


Figure 2. Effect of reaction time on 1, 4 dioxane oxidation. (Reaction conditions: 1, 4 dioxane (10 mmol), Catalyst (150 mg), 80 ˚C, 1 atm O_2).

3.5 Effect of catalyst concentration

The presence of catalyst was necessary for the progress of the reaction as in its absence only 3 % conversion of 1, 4 dioxane was observed. We changed the amount of catalyst from 110 to 190 mg while keeping the other parameters constant (Figure 3). With the increase in quantity of catalyst, we observed that the conversion of styrene increased from 45 to 85 %. Thereafter, it remained constant. However, maximum selectivity for 1, 4 dioxan-2-ol (90 %) was obtained with 150 mg of catalyst (0.045 mol % of Au). This corresponds to a turnover number of 1120 h^{-1}which is reasonably good for a heterogeneous reaction.

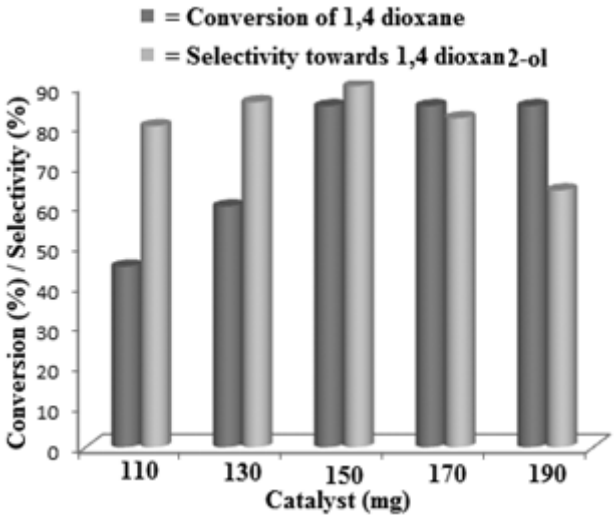


Figure 3. Effect of catalyst quantity on 1, 4 dioxane oxidation. (Reaction condition: 1, 4 dioxane (10 mmol), 80 ˚C, 24 h, 1 atm O_2.)

3.6 Recyclability of the catalyst and mechanism

Recyclability of the catalyst is one of the main advantages of a heterogeneous catalyst and an important parameter that is required for the evaluation of catalytic performance. The reusability of catalyst was evaluated by performing five consecutive oxidation reactions using the same catalyst. After each reaction the catalyst was separated from reaction mixture by filtration and frequently washed with hot DI water and ethanol to remove any sorbed organic products. After cleaning and drying, it was ready for the next batch. As shown in Figure 4, the conversion of styrene and 1, 4 dioxane remained almost constant during five consecutive cycles, which indicated the remarkable stability of the catalyst. After separation of catalyst from the reaction mixture, the filtrate was analyzed by ICP-AES for the presence of leached gold species. Reports indicate absence of measurable gold species in the filtrate.

Transmission electron microscopy is a useful tool to study the size of nanoparticles. TEM analysis of used catalyst is of considerable importance as catalytic activity of gold nanoparticles is highly size dependent. TEM pictures of the catalyst taken after the fifth cycle (Figure 5) clearly indicated that the majority of the particles were still less than 5 nm in size. No big agglomerations of nanoparticles were observed (See ESI). Therefore, we can finally

conclude that the AuNPs present in the polystyrene resin matrix are highly stable and absence of any leached AuNPs in the reaction mixture indicated that the reaction is enormously heterogeneous.

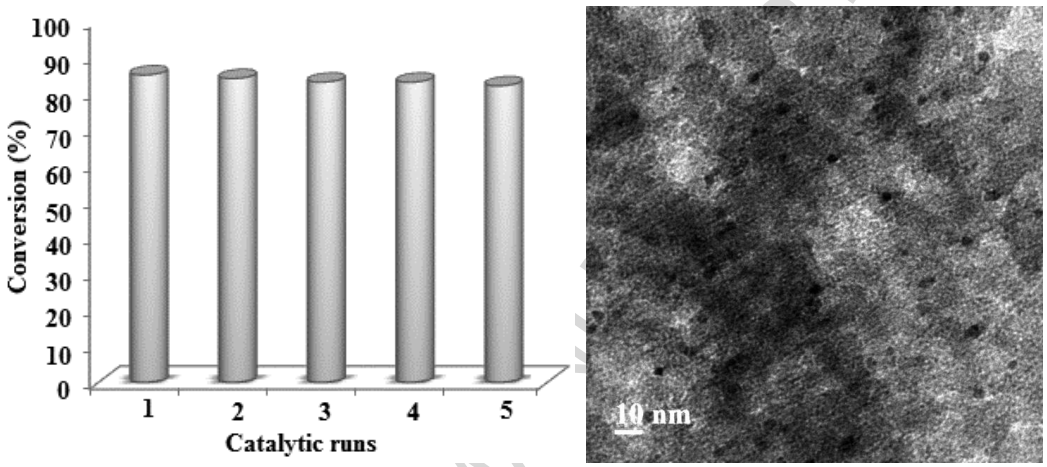


Figure 4. Recyclability of the catalyst and post reaction TEM of used catalyst

Numerous experimental and DFT studies have indicated that the surface electron density of the AuNPs is highly favorable for the adsorption of molecular oxygen and to produce active oxygen species ($\cdot O_2^-$) [27-28]. This active superoxo-like form ($\cdot O_2^-$) can abstract hydrogen from co-adsorbed reactants [29] which is 1, 4 dioxane in the present case to produce intermediate 2-hydroperoxy-1, 4-dioxane. The formed 2-hydroperoxy-1, 4-dioxane then undergoes decomposition to produce 1, 4-dioxan-2-ol and 1, 4-dioxan-2-one (Figure 5).

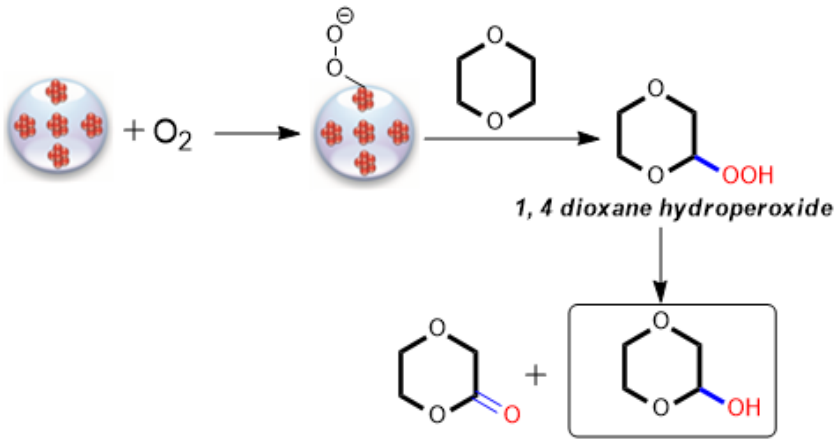


Figure 5. Schematic representation of the mechanism for aerobic oxidation of 1, 4 dioxane over Au NPs @ XAD-4 resin.

4. Conclusions

So far, oxidation of 1, 4 dioxane has not been studied much, especially, with an aim to get useful oxidation products. We are reporting for the first time gold nanoparticles catalyzed oxidation of 1, 4 dioxane. In view of above results, we can say that gold nanoparticles supported on polystyrene resin are highly active for liquid phase oxidation using molecular oxygen at low temperature with high TON. Though, pure oxygen in contact with organic liquids is potentially hazardous due to combustible nature of the reaction mixture [30], the advantages of oxygen as oxidant on environment are too many to be ignored. This study opens up a new area of aerobic C-H oxidation of saturated ethers by gold nanoparticles. A further work on oxidation of similar compounds is under progress.

Acknowledgments

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References

[1] D. Astruc, Nanoparticles and Catalysis, Wiley-VCH Verlag GmbH, Weinheim, 2008.

[2] V. Polshettiwar and T. Asefa, Nanocatalysis: Synthesis and applications, John Wiley & Sons Publication, 2013.

[3] R. A. Shedon, Chem. Commun. 2008, 3352.

[4] C. Coperet, M. Chabanas, R.P.S. Arroman, J. M. Basset, Angew. Int. Ed. 42 (2003) 156.

[5] A. S. Sharma, H. Kaur, D. Shah, RSC Adv. 6 (2016), 28688.

[6] M. Haruta, Catal. Today. 36 (1997), 153.

[7] S.A.C.Carabineiro, N. Bogdanchikova, M. A. Borja, A. Pestryakov, P. B. Tavares, J. L. Figueiredo, Nano Res. 4 (2011) 180.

[8] S. A. C. Carabineiro, N. Bogdanchikova, P. B. Tavares, J. L. Figueiredo, RSC Adv. 2 (2012) 2957.

[9] V.P.Santos, S.A.C. Carabineiro, J.J.W. Bakker, O. S. G. P. Soares, X. Chen, M. F. R. Pereira, J. J. M. Orfao, J. L. Figueiredo, J. Gascon, F. Kapteijn, J. Catal. 309 (2014) 58.

[10] S.A.C. Carabineiro, V.P. Santos, M. F.R. Pereira, J.J.M. Orfao, J. L. Figueiredo, J. Colloid Interface Sci, 480 (2016) 17.

[11] C. Marsden, E. Taarning, D. Hansen, L. Johansen, S.K. Klitgaard, K. Egeblad, C. H. Christensen, Green Chem. 10 (2008) 168.

[12] Y. Liu, H. Tsunoyama, T. Akita, S. Xie, T. Tsukuda, ACS Catal. 1 (2011) 2.

[13] S.A.C. Carabineiro, L.M.D.R.S. Martins, M. A. Borja, J.G. Buijnsters, A.J. L. Pombeiro, J. L. Figueiredo, Appl. Catal. A: Gen. 467 (2013) 279.

[14] E. M. de Moura, M. A. S. Garcia, R. V. Goncalves, P. K. Kiyohara, R. F. Jardim, L. M. Rossi, RSC Adv. 5 (2015) 15035.

[15] T. Wang, X.Yuan, S. Li, L. Zeng, J. Gong, Nanoscale. 7 (2015) 7593.

[16] J. Sun, X. Tong, Z. Liu, S. Liao, X. Zhuang, S. Xue, Catal. Comm. 85 (2016) 70.

[17] P. Howard, Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Volume II solvents, Lewis Publishers, 1991.

[18] H. Y. Kim, C. Patkar, R. Warrier, R. Kuhnb, M. Cushmana. Bioorg. Med. Chem. Lett. 15 (2005) 3207.

[19] T. Vescovi, H. M. Coleman, R. Amal, J. Hazard. Mater. 182 (2010) 75.

[20] B. K. Min, J. E. Heo, N. K. Youn, O. S. Joo, H. Lee, J. H. Kim, H. S. Kim, Catal. Comm. 10 (2009) 712.

[21] C. D. Adams, P. A. Scanlan, N. D. Secrlst, Environ. Sci. Technol. 28 (1994) 1812.

[22] C. M. Sales, A. Grostem, J. V. Parales, R. E. Parales, L. A. Cohen, Appl. Environ. Microbiol. 79 (2013) 7702.

[23] C. Ramakrishna, R. Krishna, T. Gopi, G. Sweta, B. Saini, S. C.Shekar, A. Shrivastava, Chinese Journal of Catalysis. 37 (2016) 240.

[24] P.G. Choi T. Ohno, N. Fukuhara, T. Masui, N. Imanaka, Journal of Advanced Ceramics. 4 (2015) 71.

[25] W. Fan, Y. Kubota, T. Tatsumi, Chem.Sus.Chem. 1 (2008) 175.

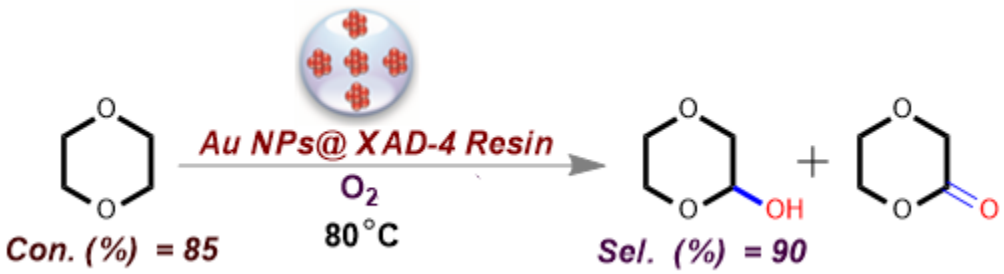
[26] D. Shah, H. Kaur, J. Mol. Catal. A: Chem. 381 (2014) 70.

[27] J. D. Stiehl, T. S. Kim, S. M. McClure, C.B. Mullins, J. Am. Chem. Soc. 126 (2004) 1606.

[28] H. L. Liu, Y. L. Liu, Y. W. Li, Z. Y. Tang, H. F. Jiang, J. Phys. Chem. C. 114 (2010) 13362.

[29] L. Wang, C. He, W. Zhang, Z. Li, J. Yang, J. Phys. Chem. C. 118 (2014) 17511.

[30] L. Vanoye, J Wang, M. Pablos, C. Bellefon, A. Favre-Réguillon, Catal. Sci. Technol., 6 (2016) 4724.



Graphical abstract

Highlights

- Au NPs@ polystyrene resin successfully used for aerobic oxidation of 1, 4 dioxane.
- High conversion (85 %) of 1,4 dioxane to 1, 4 dioxan-2-ol with 90 % selectivity.
- Green protocol with molecular oxygen as oxidant at low temperature.
- A recyclable and reusable catalyst.