

Full Paper

CuO and Ag₂O/CuO Catalyzed Oxidation of Aldehydes to the Corresponding Carboxylic Acids by Molecular Oxygen

Qingyong Tian, Daxin Shi and Yaowu Sha *

The Key Laboratory of Bioorganic Phosphorous Chemistry and Chemical Biology, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

* Author to whom correspondence should be addressed; E-mail: shayw@tsinghua.edu.cn

Received: 6 April 2008; in revised form: 17 April 2008 / Accepted: 17 April 2008 / Published: 21 April 2008

Abstract: Furfural was oxidized to furoic acid by molecular oxygen under catalysis by 150 nm-sized Ag₂O/CuO (92%) or simply CuO (86.6%). When 30 nm-size catalyst was used, the main product was a furfural Diels-Alder adduct. Detailed reaction conditions and regeneration of catalysts were investigated. Under optimal conditions, a series of aromatic and aliphatic aldehydes were oxidized to the corresponding acids in good yields.

Keywords: CuO, Ag₂O/CuO, catalyzed oxidation.

Introduction

The transformation of aldehydes to carboxylic acids is an important reaction in organic synthesis. The commonly used oxidants for this transformation are NaClO₂ [1-7], K₂Cr₂O₇ [8-9], pyridinium chlorochromate [10], quinolinium dichromate [11-13], KMnO₄ [14-16], H₂O₂ [17-18] and so on. Organic solvents such as CH₃CN, CH₂Cl₂, cyclohexane, formic acid and benzene are usually needed. Although some of them have been widely used, they still have several disadvantages: low selectivity, environmental contamination and so on. Catalytic oxidation by molecular oxygen is an eco-friendly method. However, most reported catalysts such as Ru/CeO₂ [19] and Ag₂O/Cu₂O [20] are too expensive or difficult to prepare. Comparatively, Ag₂O/Cu₂O is an economical catalyst. Even so, it

still needs to be regenerated, and there are no reports on its use for the above purpose, because it is almost impossible to keep Cu_2O unchanged at high temperature.

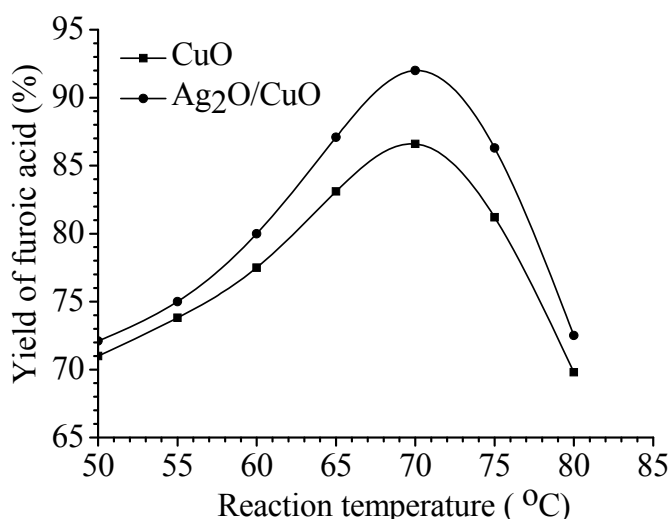
Furoic acid, an important intermediate, is mainly obtained by oxidation of furfural. A series of reagents have been developed for this reaction, such as chromium species [9, 11, 13, 21, 22] and chlorite [2, 3, 23]. For the reasons mentioned above, we first investigated the oxidation of furfural to furoic acid by oxygen catalyzed by $\text{Ag}_2\text{O}/\text{CuO}$. Detailed reaction conditions and catalyst regeneration were studied. In order to demonstrate the applicability of this method, some other aromatic aldehydes were oxidized to the corresponding aromatic carboxylic acids under optimized conditions in good yields. We also found that 150 nm-size CuO could catalyze the oxidation in a comparative yield to that obtained with an $\text{Ag}_2\text{O}/\text{CuO}$ system. This method has been used in industrial production of furoic acid.

Results and Discussion

Reaction conditions: Reaction temperature

Sodium hydroxide is needed to transform the formed acid to its salt, which is soluble in water. Otherwise the catalyst will be encapsulated by the formed acid. Aldehydes can undergo Cannizzaro reaction under basic conditions. The temperature has different effects on the kinetics of the desired oxidation and the undesired Cannizzaro reaction. Thus, it is crucial to find a suitable temperature for the reaction. As shown in Figure 1, the best temperature for both CuO and $\text{Ag}_2\text{O}/\text{CuO}$ catalyzed oxidation of furfural to furoic acid was 70°C , while higher temperatures would decrease the adsorption of oxygen and give faster side reactions.

Figure 1. Effect of reaction temperature on furoic acid yield.

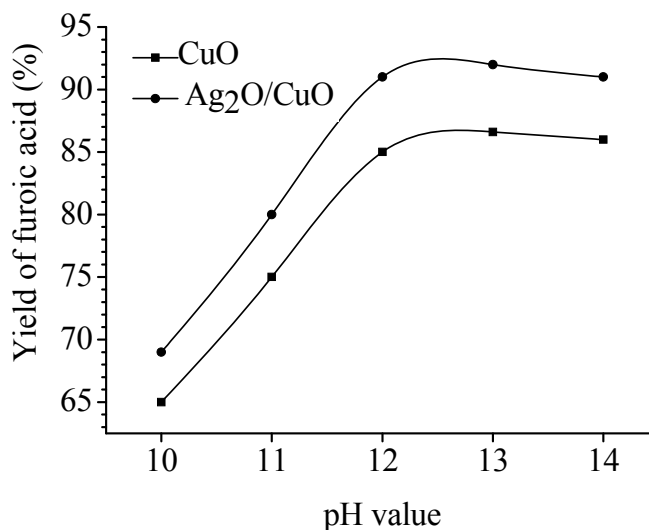


pH value

Acid can react with the catalyst to form corresponding silver and copper carboxylates which can inhibit the catalytic reaction. Therefore, it is essential to neutralize the formed acid. Meanwhile, as mentioned above, alkali will promote the undesired Cannizzaro reaction of aldehydes. The effects of

pH on the oxidation are shown in Figure 2. The optimal pH value was 13. The experiments were carried out at 70°C.

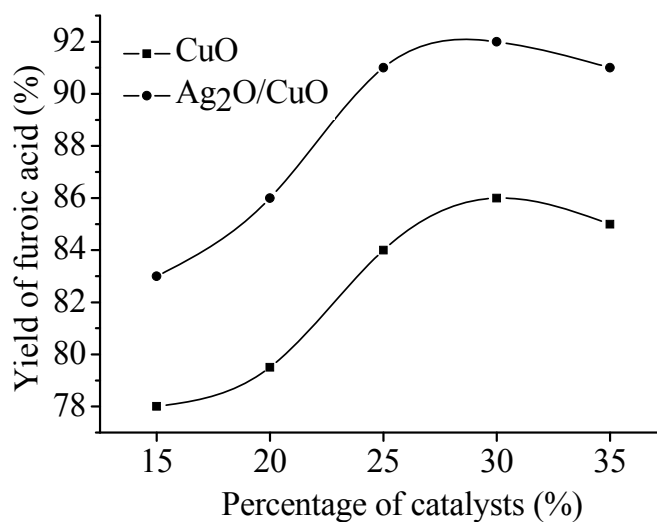
Figure 2. Effect of pH value on furoic acid yield.



Amount of catalyst

More catalyst can shorten the reaction time and raise the yield. However, the reaction rate is also controlled by other conditions, such as the distribution of oxygen. Figure 3 shows that when the catalyst was increased to 30% wt of the mixture, the yield of furoic acid reached its maximum.

Figure 3. Effect of catalyst amount on furoic acid yield.



Size of catalyst

In general, a smaller-sized catalyst will have a larger specific surface area and a better catalytic activity [24]. However, this was not the case in the $\text{Ag}_2\text{O}/\text{CuO}$ and CuO -catalyzed oxidation of furfural to furoic acid. When small nano-scale CuO and $\text{Ag}_2\text{O}/\text{CuO}$ (30 nm, Figure 4) powder were used, the main product showed a molecular weight of 300 by ESI-MS (Figure 5). Its structure is shown in Figure 6. This result suggests that small nano-scale CuO and $\text{Ag}_2\text{O}/\text{CuO}$ catalyze the Diels-Alder reaction more efficiently than the oxidation of aldehydes.

Figure 4. TEM spectra of different sizes of CuO .

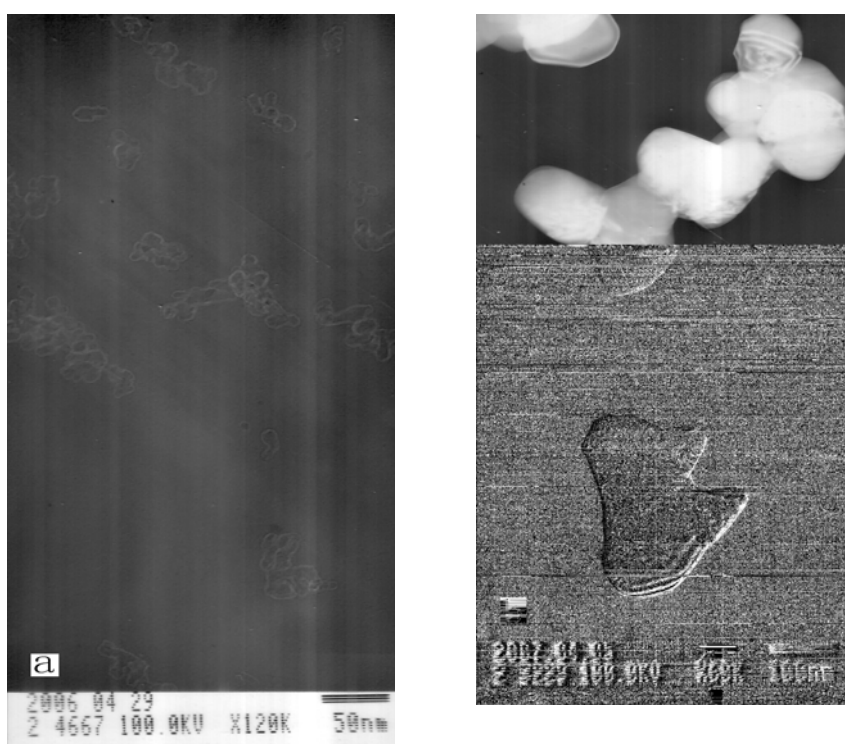


Figure 5. Mass spectrum of the Diels-Alder reaction product.

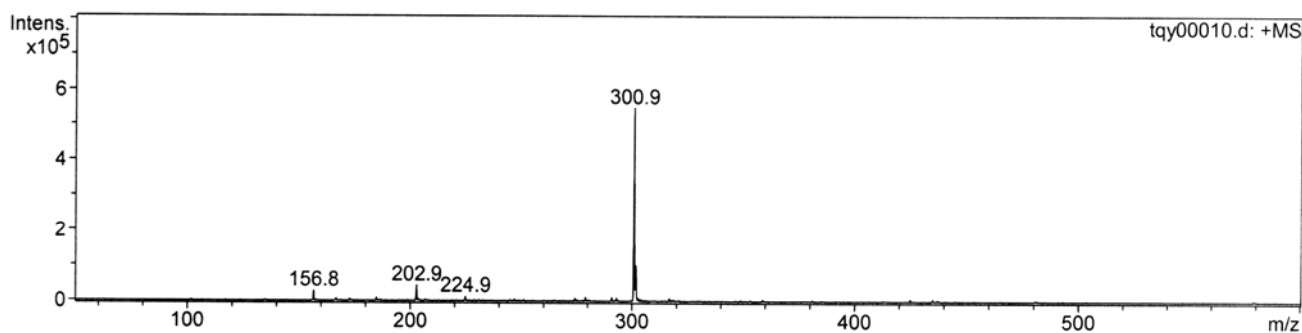
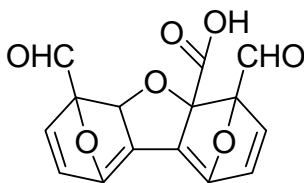


Figure 6. Product of the reaction catalyzed by 30 nm CuO and Ag₂O/CuO.*Cation poisoning*

Catalysts are always sensitive to certain cations. When deionized water was replaced with running water, no furoic acid could be obtained. Detailed experiments showed that Ca²⁺ inhibited the reaction and Mg²⁺ just made the product darker while Na⁺, K⁺, Cu²⁺ and Fe³⁺ did little harm.

Catalyst regeneration and aging

Catalyst regeneration is essential for industrial production. The recycled catalyst could not be used directly because some organic matter was adsorbed on the catalyst and part of the CuO had been reduced to Cu₂O and Cu (Figures 7 and 8). The recycled catalyst was first washed with hot deionized water to get rid of most organic adsorbates. Calcination was then performed to oxidize the reduced Cu₂O and Cu to CuO.

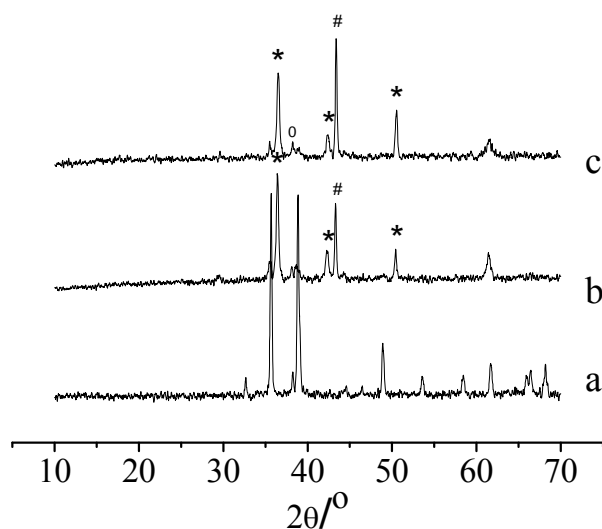
Figure 7. XRD spectra of Ag₂O/CuO; a) newly prepared; b) used 8 times; c) used 18 times; peaks with * are from Cu₂O, # are from Cu, ° are from Ag₂O.

Figure 8. XRD spectra of CuO: d) newly prepared; e) used 3 times; peaks with * are from Cu₂O, # are from Cu.

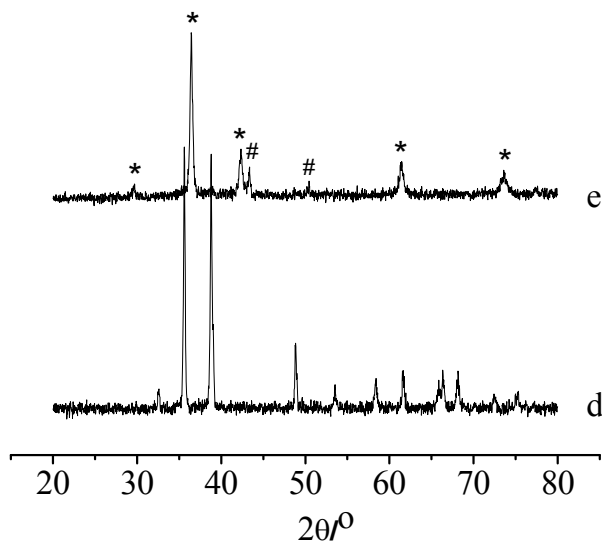
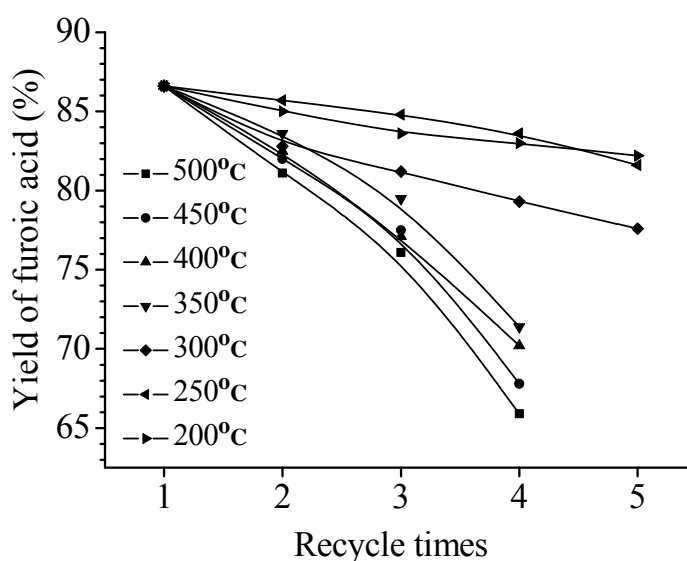


Figure 9. Effect of CuO recycling temperature on furoic acid yield.



Experiments showed that the calcination temperature greatly affected the recovery of catalyst activity and the optimal temperature was around 250 °C (Figure 9).

With recycling, the catalyst aged gradually. The product acid could erode the catalyst and cause remodeling of the catalyst surface. Calcination also caused a granular aggregate of CuO powder (Figure 10). These factors caused the specific surface area of CuO powder to decrease, so less oxygen could be adsorbed. For the Ag₂O/CuO catalyst, friction also caused Ag₂O to desquamate from the CuO (Figure 10). Therefore, the catalysts gradually became aged, as shown in Figure 11.

Figure 10. TEM spectra of the catalyst $\text{Ag}_2\text{O}/\text{CuO}$; a) used 3 times; b) used 18 times.

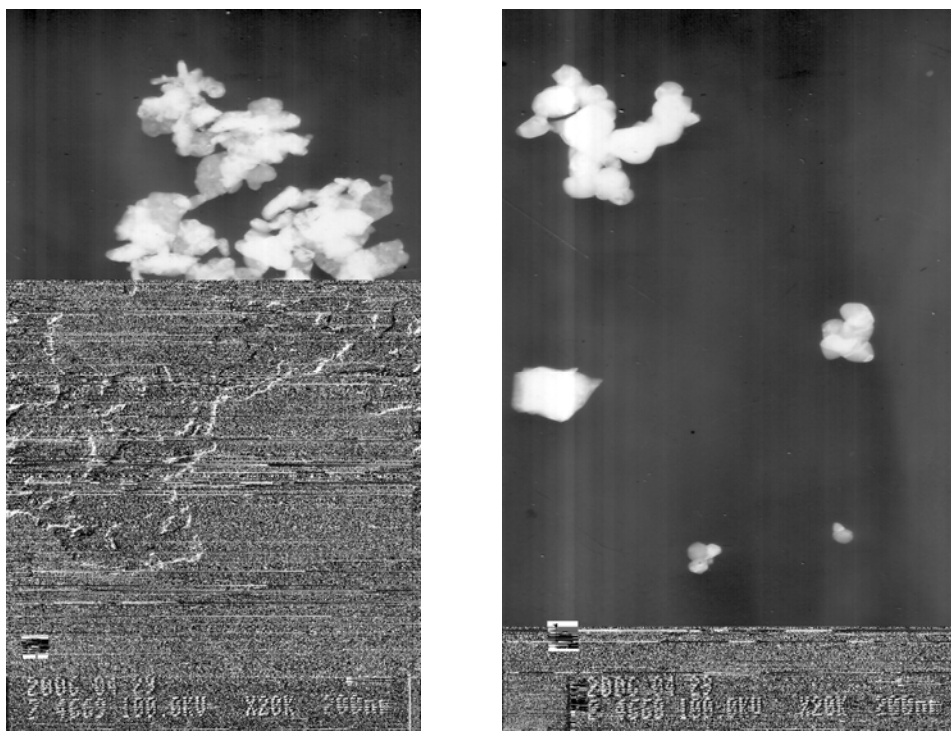
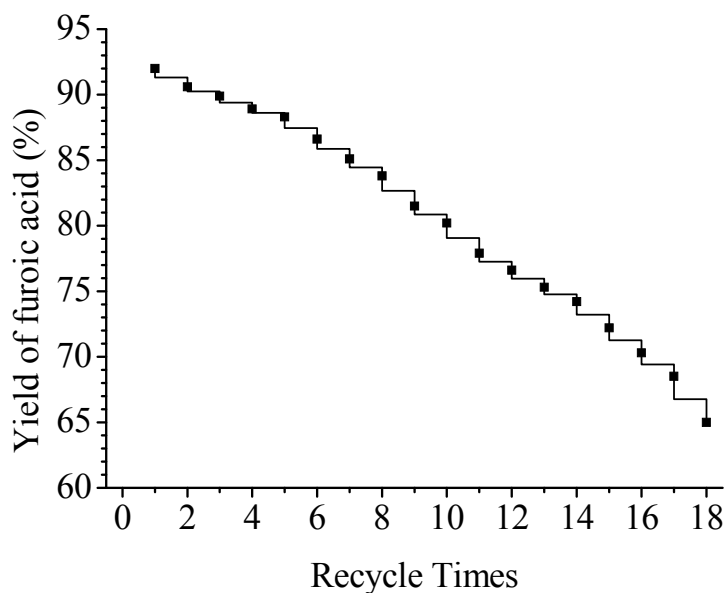


Figure 11. Effect of number of $\text{Ag}_2\text{O}/\text{CuO}$ recycling times on furoic acid yield



Application of the catalysts

$\text{Ag}_2\text{O}/\text{CuO}$ and CuO could also catalyze the oxidation of other aromatic aldehydes to their corresponding acids in good yields. $\text{Ag}_2\text{O}/\text{CuO}$ always gave better results. Comparatively, CuO has

many special advantages, such as low cost, easy preparation and regeneration. The results are shown in Table 1.

Table 1. Oxidation of aromatic aldehydes to corresponding carboxylic acids

Aldehyde	Catalyst	Yield of carboxylic acid/%
Furfural	Ag ₂ O/CuO	92.0
Furfural	CuO	86.6
Benzaldehyde	Ag ₂ O/CuO	74.5
Benzaldehyde	CuO	66.0
4-OH-3-MeO-benzaldehyde	Ag ₂ O/CuO	81.3*
4-OH-3-MeO-benzaldehyde	CuO	76.0*
4-Nitro-benzaldehyde	Ag ₂ O/CuO	78.6**
4-Nitro-benzaldehyde	CuO	71.5**
4-MeO-benzaldehyde	Ag ₂ O/CuO	73.4
4-MeO-benzaldehyde	CuO	64.2

* Ethanol was added to dissolve 4-hydroxy-3-methoxybenzaldehyde.

**Toluene was added to dissolve 4-nitrobenzaldehyde.

Conclusions

Under optimized conditions, 150 nm-size Ag₂O/CuO and CuO can catalyze the oxidation of aromatic aldehydes to their corresponding carboxylic acids by molecular oxygen in good yields. Obviously, CuO is a better choice for the industrial production in that it can be easily collected and regenerated. Small nano-scale (30 nm) CuO and Ag₂O/CuO catalysts favor Diels-Alder reactions instead of the oxidation of furfural.

Experimental

General

All chemical reagents were of analytical grade. XRD experiments were carried out on a D8 Advance Bruker X-ray Diffractometer with monochromatized CuK α ($\lambda=1.5418 \text{ \AA}$) radiation. The morphology and particle size were measured using a Hitachi H-800 transmission electron microscope (TEM). The accelerating voltage of the electron beam was 200 kV. ¹H- and ¹³C NMR spectra were recorded on a JEOL JNM ECA-300 (300 MHz) instrument. Mass spectra were obtained on a Bruker ESQUIRE-LC.

Preparation of Ag₂O/CuO

CuO (150 nm) powder (23.7 g) was added to a solution of AgNO₃ (1.83 g) in deionized water (20 mL). After stirring well for 10 minutes, the mixture was heated to vaporize the water. The precursor

was then calcined at 400 °C for 3 hours to promote the decomposition of AgNO₃. The heating rate was maintained at 5 °C/min.

Oxidation of aldehydes

To a 500 mL five-necked round bottom flask were added catalyst (5 g) and deionized water (150 mL). Solutions of NaOH (6 g) in deionized water (30 mL) and aldehyde (0.15 mol) were placed separately in two constant pressure dropping funnels. Then oxygen was blown into the flask while its contents were heated and vigorously stirred. When the temperature reached 70 °C, the NaOH aq and the aldehyde were dropped into the flask in proportional amounts. It took about 20 min to add all the reagents while the temperature was kept at 70 °C. After that, the mixture was filtered to recycle the catalyst. 30% (wt) H₂SO₄ (25 mL) was added to the filtrate while stirring. The product precipitated and was filtered, washed with water and dried. The used catalyst was first washed thoroughly with hot water to remove adsorbates. Then the catalyst was calcined for regeneration.

References and Notes

1. Zanka, A. A simple and highly practical oxidation of primary alcohols to acids mediated by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). *Chem. Pharm. Bull.* **2003**, *51*, 888-889.
2. Babu, B.R.; Balasubramaniam, K.K. Simple and facile oxidation of aldehydes to carboxylic acids. *Org. Prep. Proced. Int.* **1994**, *26*, 123-125.
3. Dalcanale, E.; Montanari, F. Selective oxidation of aldehydes to carboxylic acids with sodium chlorite-hydrogen peroxide. *J. Org. Chem.* **1986**, *51*, 567-569.
4. Bal, B.S.; Childers, W.E.; Pinnick, H.W. Oxidation of α,β -unsaturated aldehydes. *Tetrahedron* **1981**, *37*, 2091-2096.
5. Bayle, J.P.; Perez, F.; Courtieu, J. Oxidation of aldehydes by sodium chlorite. *Bull. Soc. Chim. Fr.*, **1990**, *4*, 565-567.
6. Kumaraswamy, G.; Jena, N.; Sastry, M.N.V.; Kumar, B.A. An expeditious, practical large scale synthesis of 4-amino-2-chloro-6,7-dimethoxyquinazoline. *Org. Prep. Proced. Int.* **2004**, *36*, 341-346.
7. Kamal, A.; Reddy, B.S.N.; Reddy, G.S.K.; Ramesh, G. Design and synthesis of C-8 linked pyrrolobenzodiazepine-naphthalimide hybrids as anti-tumor agents. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1933-1936.
8. Gupta, K.K.S.; Dey, S.; Gupta, S.S.; Adhikari, M.; Banerjee, A. Evidence of esterification during the oxidation of some aromatic aldehydes by chromium(VI) in acid medium and the mechanism of the oxidation process. *Tetrahedron* **1990**, *46*, 2431-2444.
9. Hurd, C.D.; Garrett, J.W.; Osborne, E.N. Furan reactions. IV. Furoic acid from furfural. *J. Am. Chem. Soc.* **1933**, *55*, 1082-1084.
10. Salehi, P.; Firouzabadi, H.; Farrokhi, A.; Gholizadeh, M. Solvent-free oxidations of alcohols, oximes, aldehydes and cyclic acetals by pyridinium chlorochromate. *Synthesis* **2001**, *15*, 2273-2276.

11. Chaubey, G.S.; Das, S.; Mahanti, M.K. Kinetics of the oxidation of heterocyclic aldehydes by quinolinium dichromate. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2215-2220.
12. Balasubramanian, K.; Prathiba, V. Quinolinium dichromate - a new reagent for oxidation of alcohols. *Indian J. Chem. Sect. B* **1986**, *25*, 326-327.
13. Chaubey, G.S.; Kharsyntiew, B.; Mahanti, M.K. Oxidation of substituted 2-furaldehydes by quinolinium dichromate: A kinetic study. *J. Phys. Org. Chem.* **2004**, *17*, 83-87.
14. Takemoto, T.; Yasuda, K.; Ley, S.V. Solid-supported reagents for the oxidation of aldehydes to carboxylic acids. *Syn. Lett.* **2001**, *10*, 1555-1556.
15. Zhivich, A.B.; Myznikov, Y.E.; Koldobskii, G.I.; Ostrovskii, V.A. XXV. Tetrazolium salts - new phase-transfer catalysts., *J. Gen. Chem. USSR (Engl. Transl.)* **1988**, *58*, 1701-1708.
16. Jursic, B. Surfactant-assisted permanganate oxidation of aromatic compounds. *Can. J. Chem.* **1989**, *67*, 1381-1383.
17. Heaney, H. Newbold, A.J. The oxidation of aromatic aldehydes by magnesium monoperoxyphthalate and urea-hydrogen peroxide. *Tetrahedron Lett.* **2001**, *42*, 6607-6610.
18. Sato, K.; Hyodo, M.; Takagi, J.; Aoki, M.; Noyori, R. Hydrogen peroxide oxidation of aldehydes to carboxylic acids: an organic solvent-, halide- and metal-free procedure. *Tetrahedron Lett.* **2000**, *41*, 1439-1442.
19. Vocanson, F.; Guo, Y.P.; Namy, J.L.; Kagan, H.B. Dioxygen oxidation of alcohols and aldehydes over a cerium dioxide-ruthenium system. *Synth. Commun.* **1998**, *28*, 2577-2582.
20. Harrison, R.J.; Moyle, M. 2-Furoic acid. *Org. Syn.* **1956**, *36*, 36.
21. Chakraborty, T.K.; Chandrasekaran, S. Facile oxidation of aldehydes to carboxylic acids with chromium(V) reagents. *Synth. Commun.* **1980**, *10*, 951-956.
22. Kharnaor, G.G.; Chaubey, G.S.; Mahanti, M.K. Kinetics of oxidation of 2-furfural by quinolinium dichromate. *Oxid. Commun.* **2001**, *24*, 377-381.
23. Moore, J.A.; Partain, E.M.III. Oxidation of furfuraldehydes with sodium chlorite. *Org. Prep. Proced. Int.* **1985**, *17*, 203-205.
24. Pan, Z.Z.; Sha, Y.W. Effect and regeneration of heterogeneous palladium/charcoal catalysts poisoned by tetramethylthiourea-quinoline in the stereoselective hydrogenation of methacycline to α -doxycycline. *Appl. Catal. A-Gen.* **2003**, *252*, 347-352.

Sample availability: Contact the authors.