Journal of Particle Science and Technology 4 (2018) 49-56

J | P | S | T

http://jpst.irost.ir

Journal of Particle Science and Technology

IROST

Application of CdO nanocatalyst in the acetylation of benzyl alcohols and degradation of sulfathiazole as a green approach

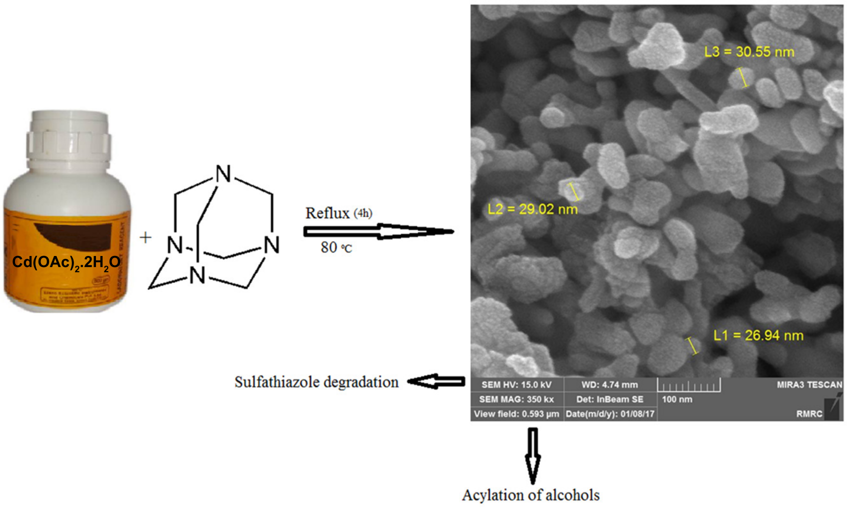
Mona Masoudinia, Azar Bagheri Ghomi*

Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran

HIGHLIGHTS

- Cadmium oxide (CdO) nanoparticles have been prepared by simple method using template of hexamine.
- A new, simple, and efficient procedure has been developed for the chemoselective acetylation of alcohols at room temperature in the presence of CdO nanoparticles.
- The presence of CdO in the UV/CdO photocatalysis system had a positive influence on the degradation of sulfathiazole.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 June 2018
Revised 24 July 2018
Accepted 14 August 2018

Keywords:

Nanospherical
CdO
Nanoparticle
Acetylation
Sulfathiazole
Degradation

ABSTRACT

In this study, CdO nanoparticles (CdO NPs) were prepared with a template. The nanoparticles were characterized by XRD, scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), and energy dispersive X-ray spectroscopy (EDX). The XRD pattern revealed that the final product has a cubic phase and its particle size diameter is 36.4 nm. The morphology of CdO is nanospherical. The catalytic activity of a CdO nanoparticle in the acetylation of benzyl alcohols was studied. The formation of products proceeds on the catalysts with predominantly strong base sites. The degradation of sulfathiazole antibiotic in the presence of CdO NPs was also investigated under ultraviolet irradiation. Various experimental parameters, such as initial sulfathiazole concentrations, initial CdO concentration and initial pH, were investigated. According to the results, this method has the potential to perform well in the removal of sulfathiazole.

** Corresponding author: Tel.: +98912-2238223 ; Fax: +9821-44600177 ; E-mail address: Azar.bagheri@iauctb.ac.ir*

DOI: 10.22104/JPST.2018.2941.1126

1. Introduction

During the past decade, interest in chemical reactions occurring at metal oxide-aqueous solution interfaces has increased significantly because of their importance in a variety of fields. These fields include atmospheric chemistry, heterogeneous catalysts and photocatalysts, chemical sensors, corrosion, environmental chemistry and geochemistry, metallurgy and ore beneficiation, metal oxide crystal growth, soil science, semiconductor manufacturing and cleaning, and tribology. Cadmium oxide (CdO) is a transparent conducting material with a direct band gap of 2.5 eV [1]. In this study, CdO was chosen as a low cost material with higher chemical stability, wide spread availability, and use in several important applications [2-8].

There have been previous reports on the synthesis of CdO NPs for nanowires and nanofilms by chemical co-precipitation or sonochemical methods [9,10]. Liu *et al.* have synthesized CdO nanoneedles by chemical vapour deposition [11]. Zou *et al.* have prepared CdO NPs using the micro-emulsion method employing anionic surfactants Aerosol-OT (AOT) reverse micelles [12].

The acetylation of −OH group provides an efficient route for the synthesis of compounds with industrial value and for the production of medicines, flavors, fragrances, solvents, food preservers, plasticizers, and cosmetics among others [13-15]. The acetylation of alcohols and phenols has been typically performed using acetic anhydride or acetyl chloride in the presence of either base [16-19] or acid catalysts [20-34]. Sulfathiazole (STZ) is extensively used in aquaculture, livestock production and also in human medicine to treat bacterial, protozoal and fungal infections [35-39]. The introduction of these compounds into the environment through anthropogenic sources can constitute a potential risk for aquatic and terrestrial organisms. Only four review articles on oxidation technologies for the removal of antibiotics in the aquatic environment have been published [40-42].

In the present work, we converted a solution of benzyl alcohol to benzyl acetate with the same selectivity as on a basic CdO catalyst to optimize the concentration of the catalyst in an aqueous solution. The other aim of this work was to investigate sulfathiazole degradation under UV irradiation. The chemical structure of the drug is given in Figure 1.

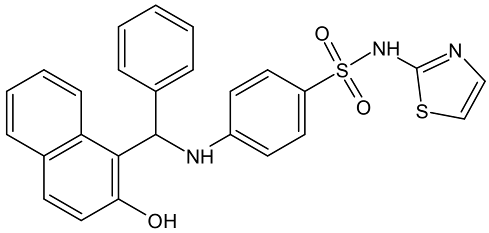


Fig. 1. The chemical structure of sulfathiazole.

2. Experimental methods

2.1. Apparatus

Phase identification of the fabricated samples was carried out with a Holland Philips X-ray diffraction CuKα (λ=1.5417 Å) in the radiation range of 20-80°. A Field emission scanning electron micrograph (SEM), Holland Philips XL30 microscope, was used to observe the morphology and elemental analysis of the samples. Spectrophotometric measurements were conducted using an UV-Vis Shimadzu 2101 spectrophotometer equipped with an Acermate 486 SX/25D computer and thermostically matched 10-mm quartz cells. Infrared spectra were recorded on a Jasco FT-IR spectrometer equipped with a liquid nitrogen-cooled HgCdTe (MCT) detector and a KBr beam splitter.

2.2. Preparation of CdO NPs

7.2 mmol (0.29 mg) NaOH was dissolved in 36 mL of distilled water under stirring. Then, 7.2 mmol (1.001 mg) of the template, hexamethylenetetramine, was added to the solution. $Cd(CH_3COO)_2.2H_2O$ (1 mmol, 0.27 mg) was added to the mixture. The mixture was refluxed for 4 h in 80 ºC. After cooling to room temperature, the precipitate was collected by filtration and washed several times with distilled water and ethanol. The CdO NPs were collected by centrifugation and drying of the precipitate at room temperature.

2.3. Procedure

For the acetylation of alcohols, a mixture of the alcohol (1 mmol), acetic anhydride (1.2 mmol, 1.5 mL) and nanocatalyst (0.08 g) in CH_2Cl_2 (10 mL) was stirred as a slurry at room temperature. The completion of the reaction, was determined by TLC, after which the mixture was filtered to recover the nanocatalyst.

The solvent was then removed under vacuum to give the crude product as a residue. The crude product was purified by column chromatography over silica gel to afford the pure desired products in high yield.

3. Results and discussion

3.1. Characterization of nanoparticles

The diffraction patterns of CdO are shown in Figure 2. The crystallite size of the prepared sample was calculated using the Scherrer formula: D = 0.9λ/β cosθ [43]. The CdO NPs have an average particle size of 36.4 nm.

The diffraction peaks values at 2θ are 33.08, 38.43, 55.31, 65.90 and 69.28° corresponding to pure CdO and matching the (111), (200), (220), (311), and (222) planes, which having a cubic structure (JCPDS Card No.05-0640). This indicates the formation of CdO NPs. Elemental analysis of the sample was performed by energy dispersive X-ray spectroscopy (EDS). The surface morphology of the prepared pure CdO was studied using SEM (Figure 2). The EDS spectra confirm the absence of impurities in the CdO NPs (Figure 3).

3.2. Optical properties

In general, the existence of impurities, synthesis method, crystalline network, and average crystal size of the semiconductor are the main factors affecting band-gap energy [44,45]. The band-gap energy of CdO has been reported to be approximately 2.9 eV. Band gap energy of the loaded samples was estimated by the Kubelka-Munk function using Eq. (1).

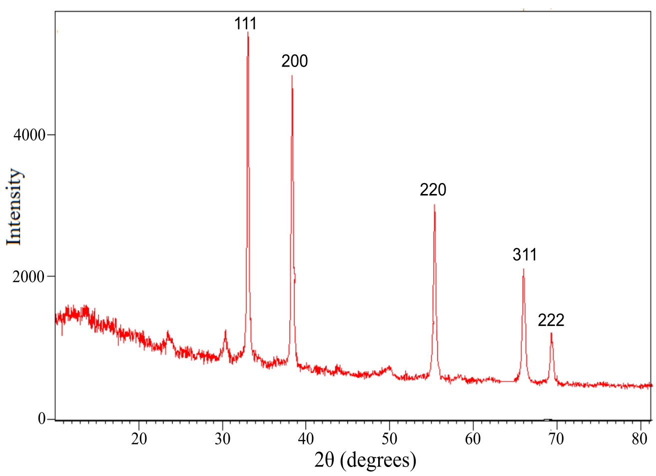


Fig. 2. XRD pattern of the synthesized CdO nanospheres.

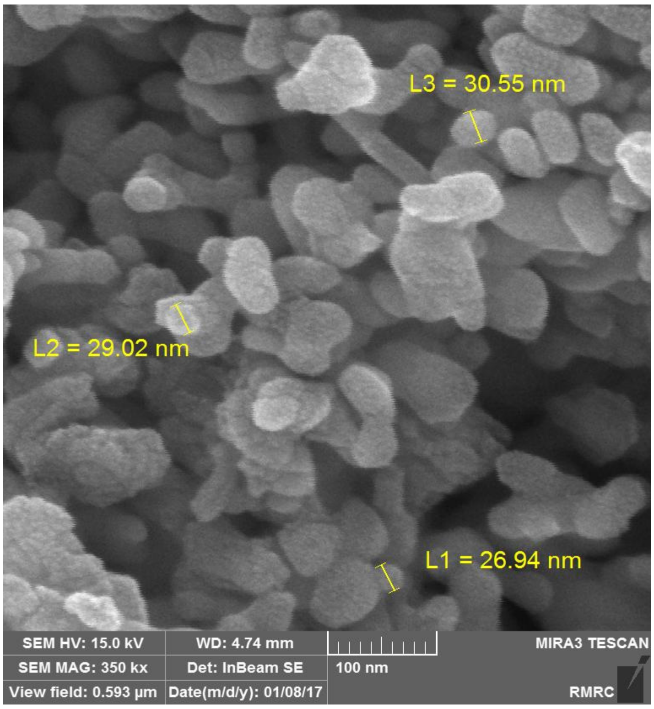


Fig. 3. SEM image of the synthesized CdO NPs.

$$(\alpha h\upsilon)^2 = \beta\,(E_g - h\upsilon)$$

Where E_g is the band gap of the proposed semiconductor (eV), h is the Planck's constant (J s), υ (or λ) is the frequency (or wavelength) of the used light (s^{-1} or nm), β is the absorption constant, and α is the absorption coefficient defined by Beer–Lambert's law as α = ([2.303×Abs]/d), where d and Abs are the sample thickness and sample absorbance, respectively. The band gap can be determined by extrapolating the linear portion of the $(\alpha h\upsilon)^2$ vs $h\upsilon$ curve. From Eq. (1), the optical band gap is determined by extrapolation of the graph to the x-axis.

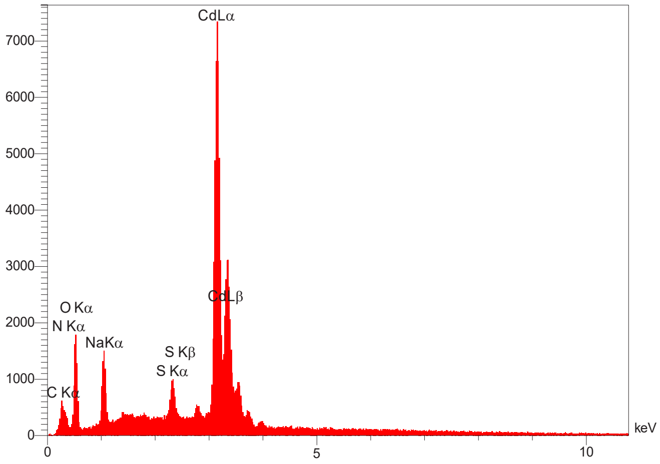


Fig. 4. Energy dispersive analysis of X-RAY (EDAX) for CdO.

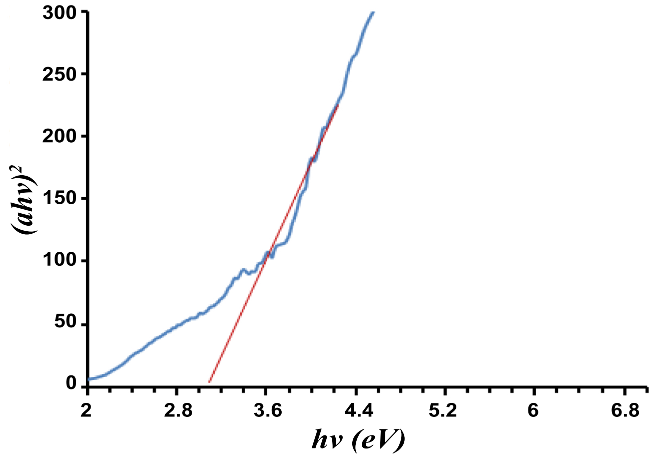


Fig. 5. Optical absorption graph of CdO.

3.3. Photocatalytic results

The efficiency of the UV/CdO photocatalytic process to remove STZ from an aqueous solution was investigated in this paper. To determine the photocatalyst effect, two experiments in the absence (Figure 5a) and presence (Figures 5b-d) of catalyst were conducted. In the absence of catalyst, the degradation of STZ was less than 15% within 2 h. The effect of different parameters, such as pH, on the STZ adsorption in CdO was also examined. A decrease in pH had a strong effect on the degradation of STZ. In the presence of CdO, the highest degradation was observed at a pH of about 3. At an acidic pH, the sulfur atom in the sulfonamide molecule can be mineralized to SO_4^{-2}, whereas the nitrogen of the molecule can be mineralized either to NH_3 or NO_2^- and/or NO_3^- [46] and these anions can give rise to a gradual decrease in pH until the molecule is degraded. It is possible that after adsorption onto CdO surface the $STZH^+$ ions take part in a direct photocatalytic process as acceptors of excited electrons. The degradation of STZ was higher than 80% within 2 h.

To investigate the effect of CdO concentration on photocatalytic efficiency, a set of experiments was performed with different concentrations of CdO in a range from 0.2–1.1 g/L. The results showed that the optimum concentration of CdO catalyst is 1.0 g/L.

Recently, mineral oxides have proven to be useful to chemists in both the laboratory and industry due to the good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier work-up and recyclability of the supports and the eco-friendly, green reaction conditions [47,48]. According to the results obtained from the metal oxides tested, TiO_2, SiO_2,

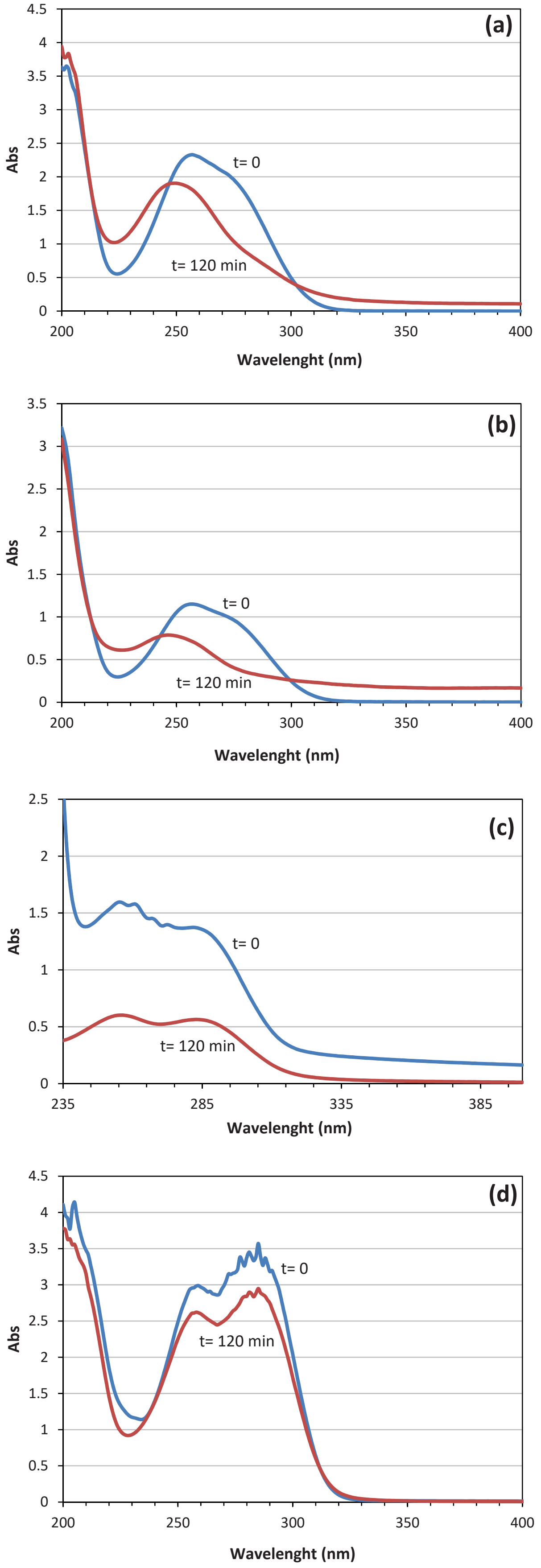


Fig. 6. Changes in the UV–Vis spectra of 30 mg/L aqueous solution of STZ in optimum conditions, during the photocatalytic process of UV/CdO with irradiation time 0-120 min: a) without catalyst, and with catalyst at b) pH= 11, c) pH= 3, and d) pH= 7.

Al_2O_3, Fe_2O_3 and Ag_2O were unable to promote benzoylation of ethanol while CaO and MgO gave large amounts of benzoic acid from the hydrolysis of the benzoyl chloride. As can be seen in Table 1, the most efficient catalyst was ZnO [49].

Herein, the performances of the CdO nanocatalyst containing different amounts of CdO were evaluated for the acetylation of alcohols. The selective acetylation of benzylic alcohols containing electron-withdrawing and electron-donating substituents with acetic anhydride was also investigated using the CdO catalyst. The results revealed that the benzylic alcohols bearing electron-donating groups have the most reactivity and are converted to the corresponding products in the shortest reaction times with the highest yield (91-98%). The possible mechanism for the acetylation of alcohols in the presence of CdO as the catalyst is shown in Scheme 1.

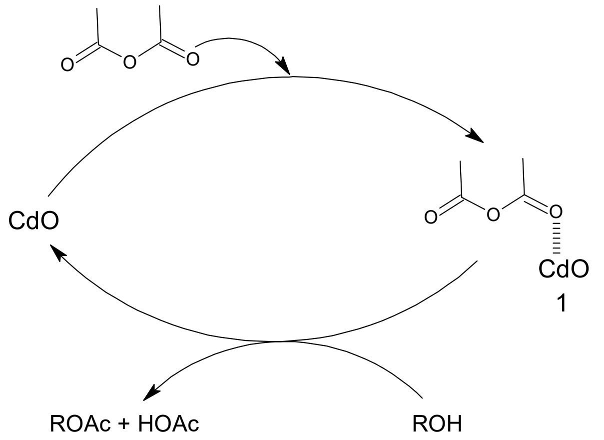
The results revealed that the best outcomes are obtained in the presence of 0.05 g of the CdO nanocatalyst at room temperature. The acetylation of benzylic alcohols was confirmed with the FT-IR spectra (Figure 7). In all of the alcohols (a-e), it can be seen that the O–H stretching vibration frequency of the alcohols is located at 3100-3300 cm^{-1}. In addition, the stretching vibrations of the carbonyl groups (C=O) of the esterification products appeared at 1650-1750 cm^{-1}.

4. Conclusions

In this paper, a simple and efficient protocol for the acetylation of alcohols was developed using a CdO nanocatalyst. The results obtained proved that for all investigated systems there is a connection between the amount of sorbed substance on the surface of the catalyst and its catalytic activity (Table 2). The proposed method has high reaction rates and excellent yields with no adverse side-reactions. The prepared nano CdO had more advantage in promoting the yields of product formation compared with other ordinary metal oxides (Table 1). Our results showed the number of atomic surfaces of nanopowder particles are a large fraction of the total; therefore, the catalytic activity of metal oxide is improved. Compared with several other catalysts reported for this transformation, the CdO nanocatalyst promoted the reaction effectively to give the desired product in high yield over a short reaction time.

Table 1. Benzoylation of ethanol with benzoyl chloride in the presence of metal oxide [49].

Entry	Metal Oxide	Time/ Temp. (h/°C)	Yield (%)
1	Al_2O_3	5/40	60
2	SiO_2	5/40	52
3	Fe_2O_3	5/40	37
4	MgO	5/40	50
5	CaO	5/40	63
6	TiO_2	5/40	24
7	Ag_2O	5/40	40
8	ZnO	5/40	93
9	Nano-ZnO	10/25	93
10	Nano-Fe_2O_3	15/25	91



Scheme 1. Proposed mechanism for the acetylation of alcohols in the presence of CdO nanocatalyst.

Since sulfonamides, including difficult biodegradable sulfa-drugs, can be removed from wastewater using the photodegradation process, oxidation of the antibiotic STZ by photolytic and photocatalytic processes using the CdO was investigated. It has been assumed that the radical pathway is a dominant mode of STZ degradation in the combined UV photolysis system. Our experiments have shown that the presence of CdO in the UV/CdO photocatalysis system had a positive influence on the degradation of STZ. The results showed that the system is most efficient at 30 mg/L and 0.02 g/L concentrations of STZ and CdO nanoparticles in acidic conditions, respectively.

Acknowledgments

We wish to thank the Islamic Azad University Central Tehran Branch for its invaluable support throughout the project.

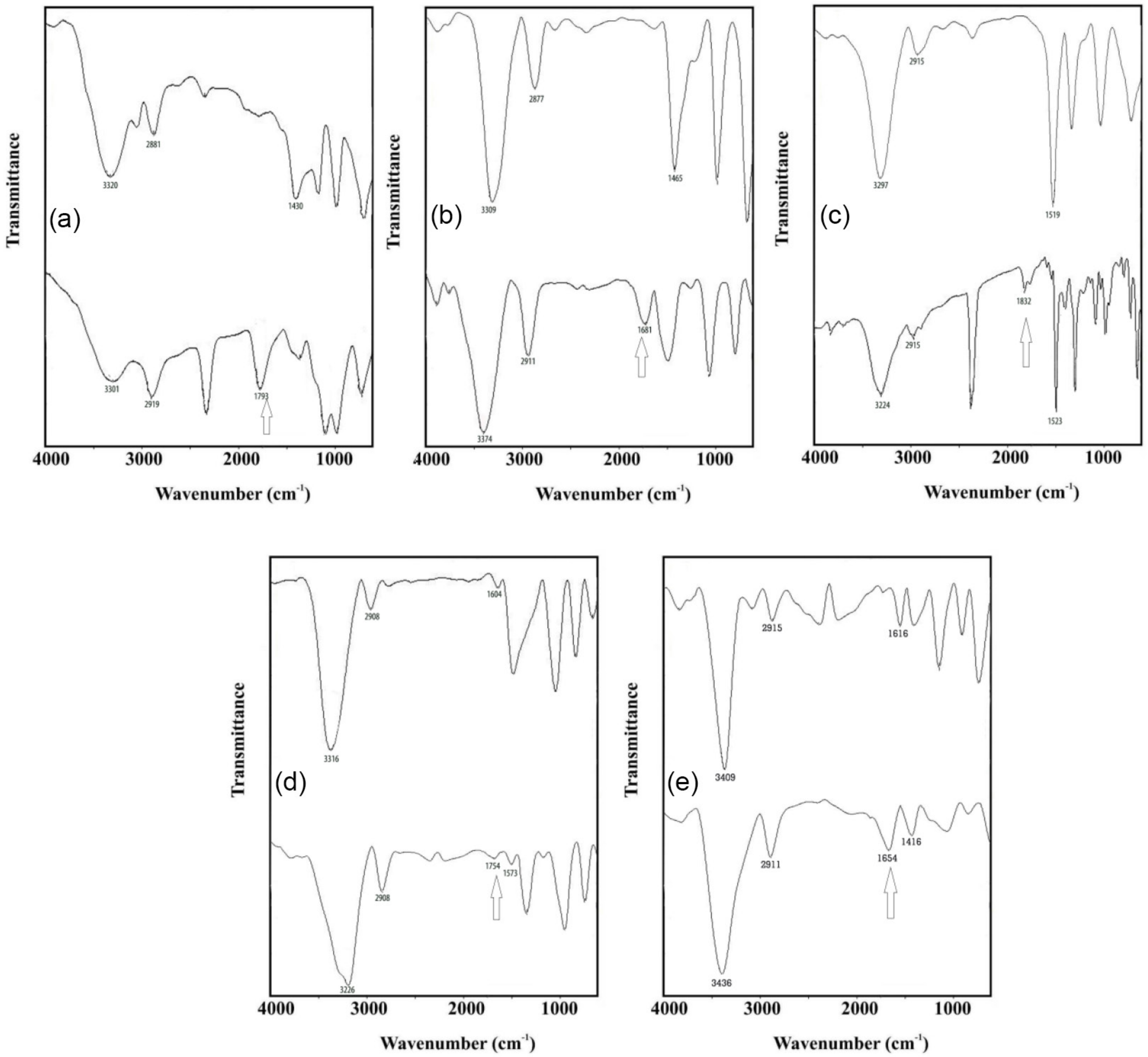


Fig. 7. FT-IR spectra of a) benzyl alcohol, b) 2-methyl benzyl alcohol, c) 2-nitro benzyl alcohol, d) 4-chloro-benzyl alcohol, and e) 4-hydroxy-benzyl alcohol and corresponding esteric products. In all figures the stretching vibrations of carbonyl groups (C=O) of corresponding products are shown with arrows.

Table 2. Selective acetylation of benzyl alcohols in the presence of different concentrations of CdO nanocatalyst.

Substrate	product	Reaction time (30 mg)	Reaction time (50 mg)	Reaction time (70 mg)	Yield (%)
$C_6H_5CH_2OH$	$C_6H_5CH_2OAc$	15	10	10	98
p-Cl-C_6H_4-CH_2OH	*p*-Cl-C_6H_4-CH_2OAc	55	30	40	94
o-NO_2-C_6H_4-CH_2OH	*o*-NO_2-C_6H_4-CH_2OAc	70	45	50	91
o-CH_3-C_6H_4-CH_2OH	*o*-CH_3-C_6H_4-CH_2OAc	20	20	20	96
p-OH-C_6H_4-CH_2OH	*p*-OH-C_6H_4-CH_2OAc	20	10	5	92

Reaction conditions: alcohol 1 mmol, acetic anhydride 1.2 mmol, catalyst 0.03, 0.05 and 0.07 g, room temperature, CH_2Cl_2 as solvent.

References

[1] A.J. Varkey, A.F. Fort, Transparent conducting cadmium oxide thin films prepared by a solution growth technique, Thin Solid Films, 239 (1994) 211-213.

[2] M.A. Grado-Caffaro, M. Grado-Caffaro, A quantitative discussion on band-gap energy and carrier density of CdO in terms of temperature and oxygen partial pressure, Phys. Lett. A, 372 (2008) 4858-4860.

[3] F. Yakuphanoglu, Nanocluster n-CdO thin film by sol-gel for solar cell applications, Appl. Surf. Sci. 257 (2010) 1413-1419.

[4] A.S. Kamble, R.C. Pawar, J.Y. Patil, S.S. Suryavanshi, P.S. Patil, From nanowires to cubes of CdO: Ethanol gas response, J. Alloy. Compd. 509 (2011) 1035-1039.

[5] R.K. Gupta, K. Ghosh, R. Patel, P.K. Kahol, Low temperature processed highly conducting, transparent, and wide bandgap Gd doped CdO thin films for transparent electronics, J. Alloy. Compd. 509 (2011) 4146-4149.

[6] G. Singh, I. P.S. Kapoor, R. Dubey, P. Srivastava, Synthesis, characterization and catalytic activity of CdO nanocrystals, Mater. Sci. Eng. B-Adv. 176 (2011) 121-126.

[7] J. Li, Y. Ni, J. Liu, J. Hong, Preparation, conversion, and comparison of the photocatalytic property of $Cd(OH)_2$, CdO, CdS and CdSe, J. Phys. Chem. Solids, 70 (2009) 1285-1289.

[8] A.A. Dakhel, Influence of annealing in nitrogen on the structural, electrical, and optical properties of CdO films doped with samarium, Mater. Chem. Phys. 117 (2009) 284-287.

[9] C. Qiu, X. Xiao, R. Liu, Biomimetic synthesis of spherical nano-hydroxyapatite in the presence of poly ethylene glycol, Ceram. Int. 34 (2008) 1747-1751.

[10] A. Askarinejad, A. Morsali, Syntheses and characterization of $CdCO_3$ and CdO nanoparticles by using a sonochemical method, Mater. Lett. 62 (2008) 478-482.

[11] Y. Liu, C. Yin, W. Wang, Y. Zhan, G. Wang, Synthesis of cadmium oxide nanowires by calcining precursors prepared in a novel inverse microemulsion, J. Mater. Sci. Lett. 21 (2002) 137-139.

[12] B.S. Zou, V.V. Volkov, Z. Wang, Optical properties of amorphous ZnO, CdO, and PbO nanoclusters in solution, Chem. Mater. 11 (1999) 3037-3043.

[13] L. Osiglio, G. Romanelli, M. Blanco, Alcohol acetylation with acetic acid using borated zirconia as catalyst, J. Mol. Catal. A-Chem. 316 (2010) 52-58.

[14] T.W. Green, P.G.M. Wutz, Protective Groups in Organic Synthesis, 2nd ed., Wiley, New York, 1991.

[15] P. Kumar, R. Pandey, M. Bodas, S. Dagade, M. Dongare, A. Ramaswamy, Acylation of alcohols, thiols and amines with carboxylic acids catalyzed by yttria-zirconia-based Lewis acid, J. Mol. Catal. A-Chem. 181 (2002) 207-213.

[16] W. Steglich, G. Hofle, N,N-Dimethyl-4-pyridin amine, a very effective acylation catalyst, Angew. Chem. Int. Edit. 8 (1969) 981.

[17] E. Vedejs, S.T. Diver, Tributylphosphine: a remarkable acylation catalyst, J. Am. Chem. Soc. 115 (1993) 3358-3359.

[18] E.F.V. Scriven, 4-Dialkylaminopyridines: super acylation and alkylation catalysts, Chem. Soc. Rev. 12 (1983) 129-161.

[19] S. Tomohumi, O. Kousaburo, O. Takashi, Remarkably fast acylation of alcohols with benzoyl chloride promoted by TMEDA, Synthesis, (1999) 1141-1144.

[20] A. Orita, C. Tanahashi, A. Kakuda, J. Otera, Highly efficient and versatile acylation of alcohols with $Bi(OTf)_3$ as catalyst, Angew. Chem. Int. Edit. 39 (2000) 2877-2879.

[21] R. Alleti, M. Perambuduru, S. Samanha, V.P. Reddy, Gadolinium triflate: an efficient and convenient catalyst for acetylation of alcohols and amines, J. Mol. Catal. A-Chem. 226 (2005) 57-59.

[22] I. López, J.L. Bravo, M. Caraballo, J.L. Barneto, G. Silvero, Task-oriented use of ionic liquids: efficient acetylation of alcohols and phenols و Tetrahedron, 52 (2011) 3339-3341.

[23] B. Karimi, J. Maleki, Lithium Trifluoromethane-sulfonate (LiOTf) as a recyclable catalyst for highly efficient acetylation of alcohols and diacetylation of aldehydes under mild and neutral reaction conditions, J. Org. Chem. 68 (2003) 4951-4954.

[24] N. Ahmed, J.E. van Lier, Molecular iodine in isopropenyl acetate (IPA): a highly efficient catalyst for the acetylation of alcohols, amines and phenols under solvent free conditions, Tetrahedron Lett. 47 (2006) 5345-5349.

[25] R.H. Tale, R.N. Adude, A novel 3-nitrobenzene

boronic acid as an extremely mild and environmentally benign catalyst for the acetylation of alcohols under solvent-free conditions, Tetrahedron Lett. 47 (2006) 7263-7265.

[26] T.S. Reddy, M. Narasimhulu, N. Suryakiran, K.C. Mahesh, K. Ashalatha, Y. Venkateswarlu, A mild and efficient acetylation of alcohols, phenols and amines with acetic anhydride using $La(NO_3)_3 \cdot 6H_2O$ as a catalyst under solvent-free conditions, Tetrahedron Lett. 47 (2006) 6825-6829.

[27] P. Phukan, Iodine as an extremely powerful catalyst for the acetylation of alcohols under solvent-free conditions, Tetrahedron Lett. 45 (2004) 4785-4787.

[28] R. Dalpozzo, A. De Nino, L. Maiuolo, A. Procopio, M. Nardi, G. Bartoli, R. Romeo, Highly efficient and versatile acetylation of alcohols catalyzed by cerium(III) triflate, Tetrahedron Lett. 44 (2003) 5621-5624.

[29] A. Kamal, M.N.A. Khan, K.S. Reddy, Y.V.V. Srikanth, T. Krishnaji, $Al(OTf)_3$ as a highly efficient catalyst for the rapid acetylation of alcohols, phenols and thiophenols under solvent-free conditions, Tetrahedron Lett. 48 (2007) 3813-4818.

[30] S. Velusamy, S. Borpuzari, T. Punniyamurthy, Cobalt(II)-catalyzed direct acetylation of alcohols with acetic acid, Tetrahedron Lett. 61 (2005) 2011-2015.

[31] G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantoni, M. Massaccesi, L. Sambri, $Zn(ClO_4)_2 \cdot 6H_2O$ as a powerful catalyst for a practical acylation of alcohols with acid anhydrides, Eur. J. Org. Chem. 32 (2003) 4611-4617.

[32] N. Ghaffari Khaligh, Preparation, characterization and use of poly(4-vinylpyridinium) perchlorate as a new, efficient, and versatile solid phase catalyst for acetylation of alcohols, phenols and amines, J. Mol. Catal. A-Chem. 363 (2012) 90-100.

[33] F. Rajabi, A heterogeneous cobalt(II) Salen complex as an efficient and reusable catalyst for acetylation of alcohols and phenols, Tetrahedron Lett. 50 (2009) 395-397.

[34] L. Osiglio, A.G. Sathicq, G.P. Romanelli, M.N. Blanco, Borated zirconia modified with ammonium metatungstate as catalyst in alcohol acetylation, J. Mol. Catal. A-Chem. 359 (2012) 97-103.

[35] A.K. Sarmah, M.T. Meyer, A.B.A. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere, 65 (2006) 725-759.

[36] T. Schwartz, W. Kohnen, B. Jansen, U. Obst, Detection of antibiotic-resistant bacteria and their resistance genes in wastewater, surface water, and drinking water biofilms, FEMS Microbiol. Ecol. 43 (2003) 325-335.

[37] T. Schwartz, H. Volkmann, S. Kirchen, W. Kohnen, K. Schon-Holz, B. Jansen, U. Obst, Real-time PCR detection of Pseudomonas aeruginosa in clinical and municipal wastewater and genotyping of the ciprofloxacin-resistant isolates, FEMS Microbiol. Ecol. 57 (2006) 158-167.

[38] M. Seifrtová, A. Pena, C.M. Lino, P. Solich, Determination of fluoroquinolone antibiotics in hospital and municipal wastewaters in Coimbra by liquid chromatography with a monolithic column and fluorescence detection, Anal. Bioanal. Chem. 391 (2008) 799-805.

[39] S. Jiao, S. Zheng, D. Yin, L. Wang, L. Chen, J. Environ. Sci. 20 (2008) 806-813.

[40] K. Kümmerer, Antibiotics in the aquatic environment- A review - Part I, Chemosphere, 75 (2009) 417-434.

[41] M. Klavarioti, D. Mantzavinos, D. Kassino, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402-417.

[42] V.K. Sharma, Oxidative transformations of environmental pharmaceuticals by Cl_2, ClO_2, O_3, and Fe(VI): Kinetics assessment, Chemosphere, 73 (2008) 1379-1386.

[43] M.E. Fragalà, Y. Aleeva, G. Malandrino, Effects of metal-organic chemical vapour deposition grown seed layer on the fabrication of well aligned ZnO nanorods by chemical bath deposition, Thin Solid Films, 519 (2011) 7694-7701.

[44] N. Chopra, A. Mansingh, G.K. Chadha, Electrical, optical and structural properties of amorphous V_2O_5–TeO_2 blown films, J. Non-cryst. Solids, 126 (1990) 194-201.

[45] F.A. Harraz, R.M. Mohamed, A. Shawky, I.A. Ibrahim, Composition and phase control of Ni/NiO nanoparticles for photocatalytic degradation of EDTA, J. Alloy. Compd. 508 (2010) 133-140.

[46] P. Calza, C. Medana, M. Pazzi, C. Baiocchi, E. Pelizzetti, Photocatalytic transformations of sulphonamides on titanium dioxide, Appl. Catal.

B-Environ. 53 (2004) 63-69.

[47] M.H. Sarvari, H. Sharghi, Reactions on a solid surface. A Simple, economical and efficient Friedel-Crafts acylation reaction over zinc oxide (ZnO) as a new catalyst, J. Org. Chem. 69 (2004) 6953-6956.

[48] R.S. Varma, Solvent-free organic syntheses. Using supported reagents and microwave irradiation, Green Chem. 1 (1999) 43-45.

[49] J. Otera, Esterification: Methods, Reactions, and Applications, 1st ed., Wiley-VCH, Weinheim, 2003.