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Ag-doped TiO_2 enhanced photocatalytic oxidation of 1,2-cyclohexanediol†

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The superiority of silver-doped titania for photocatalytic oxidation (PCO) of organic compounds inspired us to investigate PCO of 1,2-cyclohexanediol. Ag/TiO_2 was prepared, characterized (nanosize 19–24 nm) and used for oxidation of 1,2-cyclohexanediol (1) in acetonitrile. The photolysate was analyzed using GC and GC/MS techniques. The PCO products are 2-hydroxylcyclohexanone (2), 1,2-cyclohexandione (3), 2-cyclohexenone(4), cyclohexanone (5), and adipic acid (6).The formation of electron–hole pair at the surface of the catalyst followed by oxidation reactions was the suggested mechanism. Kinetic studies revealed first-order mechanism for PCO of 1 and rate constant (k) = $-0.145\ h^{-1}$. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: Ag /TiO_2 nanoparticle; 1,2-Cyclohexanediol; photocatalysis; photocatalytic oxidation

INTRODUCTION

Heterogeneous photocatalysis has been started with the pioneer findings of Fujishima and Honda.[1] Application of photocatalytic oxidation (PCO), as one of the promising technologies, in water recycling, air pollution treatment,[2–14] as well as in organic synthesis,[15–22] has been a great interest. The need for sustainable green chemistry technology to obtain valuable chemicals appears today of primary importance. PCO may decisively contribute to this target, but a main drawback is that TiO_2 is a UV absorber and has to be modified to make use of the renewable solar energy. In this domain, extensive work has been carried out to enhance the anatase PCO activity via deposition of noble metals (Ag, Au, Pt), non-noble metals (Cu, Zn, Fe, Pd, W, Co, Rb, Y, La, Mo), or other elements(N, C, S, F, P).[5–12]

Several factors have a role on the rate of PCO process, such as type and size of TiO_2 particles, silver precursor, method of preparation of the doped catalyst, nature of the substrate, the pH, and the rate of oxygen flow.[7] Ag deposits generate a great number of holes by acting as electron sinks and assisting their transfer to species in solution (e.g., dissolved O_2). This reduces the possibility of electron/hole recombination. The organic compound must be adsorbed on the semiconductor catalyst surface for photo-generated holes are capable of direct oxidation at pH lower than the point of zero charge of the catalyst.

Continuing our interest on PCO of cyclic and acyclic alcohols,[17,20,21] as well as other interests on PCO of biomolecules,[23–26] the present article embraces PCO of 1,2-cyclohexanediol (**1**). Cyclohexane moiety represents the base structure of many biomolecules such as sterols and estrogens hormones (estriol). So, selective PCO of **1** to the corresponding carbonyl derivatives has a great significance and is of interest.

EXPERIMENTAL

Materials

Acetonitrile (HPLC grade), cyclohexanone, and adipic acid were purchased from Aldrich; 1,2-cyclohexanediol (**1**, 98%) was obtained from Alfa Aeser GmbH & Co and 1,2-cyclohexanedione (**3**) from Merck Schuchardt.

Preparation of 2-hydroxycyclohexanone (2)

A solution of dimethyl adipate (4.0 g, 0.23 mole) in 40-ml dry toluene was added for 1 h to a mixture of freshly wired sodium metal (2.3 g, 0.1 gA) in 120-ml dry toluene placed in a three-necked flask. The reaction was processed as reported.[27] Colorless crystals of **2** were obtained (1.2 g, 47%). The circumstances were as follows: mp 95–98 °C, lit. mp = 93–98 °C,[27] mass spectra, m/z (%) = 114 (26, $P^{+\cdot}$), 70 (100, $B^{+\cdot}$).

Preparation of 2-cyclohexenone (4)

A solution of 15 g chromic anhydride in a mixture of 15-ml water and 50-ml glacial acetic acid was dropwise added to a mixture of 13.66 g (0.16 M) cyclohexane in 33.0 g glacial acetic acid placed in a three-necked flask at 25–35 °C. The reaction was processed as reported.[28] The product 2-cyclohexane (3.3g, 37%) was collected at 55–56 °C/17 mm Hg, lit. bp 67 °C/25 mm Hg,[28] and mass spectra, m/z (%) = 96 (46, $P^{+\cdot}$), 68 (100, $B^{+\cdot}$).

Preparation of Ag/TiO_2 catalyst. The catalyst Ag/TiO_2 (1%, w:w) was prepared from TiO_2 (Degussa P25), and the aqueous solution of $AgNO_3$ was prepared as reported by the impregnation method.[8,29] A mixture of TiO_2 (1.0 g, Degussa P25) and $AgNO_3$ (0.0157 g) in 5 ml bidistilled

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water was magnetically stirred for 48 h at room temperature; after that, the water was removed at 100 °C. Finally, the solid residue was calcined at 500 °C for 5 h, according to the literature procedure.[8,29]

Instrumentation

The electronic absorption spectra were recorded on UV-2101 PC, UV–vis Spectrophotometer (Shimadzu). GC analyses were performed employing Perkin Elmer, Auto System XLGC using capillary column (30 m × 2.23 mm) packed with 5% diphenyl–95% dimethyl polysiloxane and 0.25 μm film thicknesses. GC/MS analysis was carried out using GC model: GC 2000 thermo, capillary column DB-5 (5% phenyl–95% methyl polysiloxane), 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness.

Photoreactor

All the photocatalytic reactions were carried out in a Vycor glass cell (29.5 × 2.5 cm), fitted with a reflux condenser capped with $CaCl_2$ drying tube, and externally irradiated with a 450 W medium pressure mercury lamp (ACE glass, immersion type) with a Pyrex well, which has maximum emission at 296.7–578 nm (4.18–2.15 eV; Fig. 1).The distance between the sample cell and the radiation source is 5 cm. The system was covered with aluminum foil served as light reflector to decrease light loss, and the apparatus was set up in a metallic cabinet.[21]

General procedure of photocatalytic experiment

A 75-ml solution (0.1 M) of 1,2-cyclohexanediol (**1**) was prepared in dry acetonitrile, 75 mg of Ag/TiO_2 was added to the solution, and the mixture was transferred to the reaction vessel and sonicated in an ultrasonic bath for 15 min. The stirred suspension was bubbled with a stream of oxygen gas (at a flow rate of 30 ml/min) and then illuminated for 20 h. The reaction progress was monitored by GC at different intervals. After irradiation, the titanium dioxide powder was removed by filtration using a medium-porosity frit, and the solvent was evaporated by using rotatory evaporator.[20] The reaction mixture was analyzed by GC and GC/MS techniques using authentic samples

RESULTS AND DISCUSSION

The selectivity of Ag/TiO_2 catalyst was demonstrated for enhancement of PCO of organic compounds, which are predominantly oxidized by holes.[4,7] This advantage was applied for the PCO of the target compound 1,2-cyclohexanediol. The silver-doped titanium dioxide was prepared as reported[8] and characterized using transmission electron microscopy (TEM). TEM indicated the formation of Ag/TiO_2 particles in nanoscale size of 19–24 nm (Fig. 2). The silver loading was 1% (w: w), and the optimum concentration was reported by Liu *et al.*[30]

TEM results

The TEM micrograph of Ag/TiO_2 showed uneven distribution of Ag on TiO_2. The loaded silver covers only part of the TiO_2 surface, and the silver cluster differed as silver loading varied (Fig. 2).

Results of photocatalysis

Silver deposits generate a number of holes by acting as electron sinks and assisting their transfer to the dissolved oxygen species in solution forming the superoxide $O^{\cdot-}$. This reduces the e^-/h^+ recombination possibilities and therefore enhances the oxidation–reduction process.

Analysis of the photolysate mixtures using GC and GC/MS techniques revealed that the percentage conversions of 1,2-cyclohexanediol are 41%, 61%, 83%, and 95% after irradiation for 5, 10, 15, and 20 h, respectively (Fig. 3). Also, the products after irradiation for 20 h included 2-hydroxylcyclohexanone (**2**, 24%), 1,2-cyclohexanedione (**3**, 26%), 2-cyclohexenone (**4**, 8%), and cyclohexanone (**5**, 5%), in addition to the acyclic acidic oxidation product adipic acid (**6**, 10%).

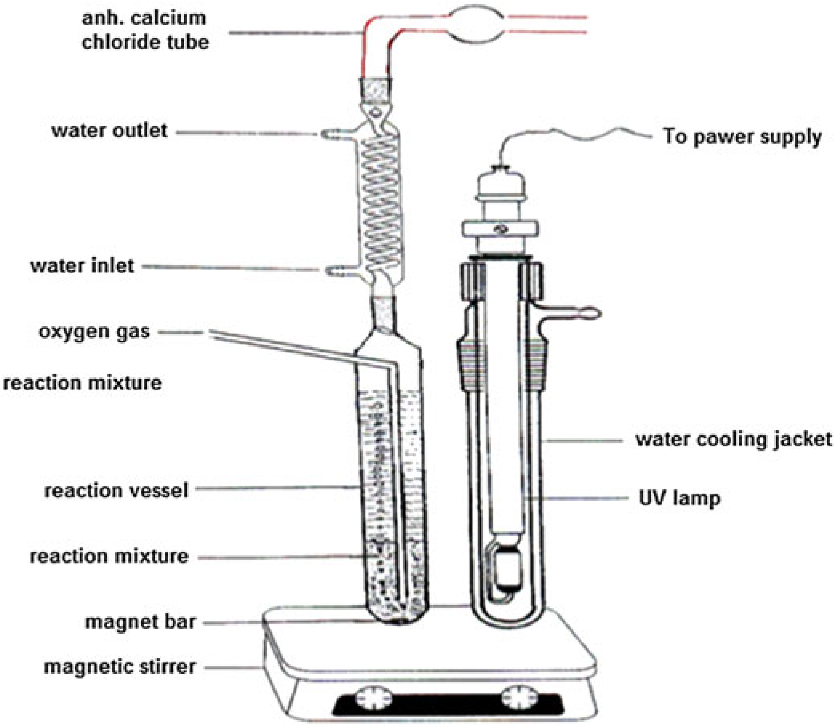


Figure 1. The photocatalysis system

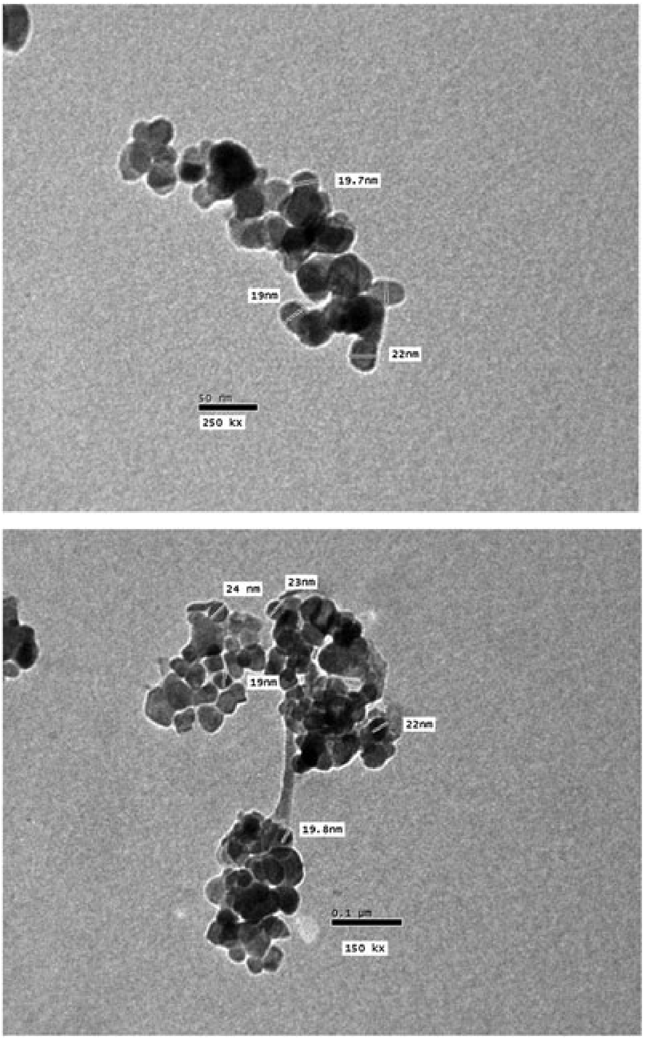


Figure 2. TEM images of Ag/TiO_2

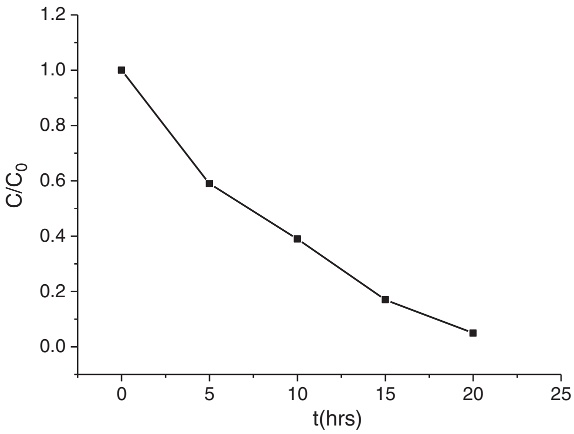


Figure 3. Photocatalytic disappearance of **1** in acetonitrile

Reaction mechanisms

The reaction mechanism (Scheme 1) has been proposed depending on the reaction products and conditions. The target 1,2-cyclohexanediol (**1**) is a sensitive probe; when adsorbed at the Ag/TiO_2–acetonitrile interface, it traps the holes, forming the radical cation 1_a via single electron transfer, which is rapidly deprotonated to form the α-hydroxyl radical 1_b.

Formation of **2**, **3**, **4**, and **5** may be suggested starting from 1_b via three different routes (A, B, and C). Route A takes place via a second electron oxidation of 1_b with generation of the protonated carbonyl intermediate 1_C, which in turn transfers to 2 via a proton loss. The second route (B) embraces trapping of O2$^-$ with the formation of the peroxy anion radical 1_d. Also, trapping of O_2 gives the peroxy radical 1e. Decomposition of 1_d and 1_e would be expected to occur rapidly to form the cyclic oxidation products **2**, **3**, **4**, and **5**.[31] Formation of **4** could be expected via dehydration of **2**.[21,32] A multistep process (scheme 20) may be proposed for the formation of **5** from **2**.[33] Furthermore, open-chain carbonyl compounds such as adipic acid (**6**) can be produced by single electron mechanism via ring rupture of 1_a to 1_g with a proton loss (route D).

The use of water-free acetonitrile solvent rules out the participation of hydroxyl radicals in the photocatalyzed oxidation process and the elimination of the metal (Ag) by photocorrosion. Acetonitrile, as a polar nonhydroxylic solvent, represents the best solvent for controlling the oxidation reactivity at the interface, between a liquid reaction and a solid irradiated photocatalyst.[19–22] Also, direct photolysis is excluded as the λ_{max} of 1,2-cyclohexanediol was observed at 224 nm ($\epsilon = 2.28$ mV), whereas the maximum emission of the used 450-Wt medium pressure Hg lamp is in the range 296.7–578.0 nm. Accordingly, the obtained products obviously originated through initial band gap excitation of the Ag/TiO_2 catalyst rather than substrate **1**.

Also, no oxidation products could be detected upon irradiation of 1,2-cyclohexanediol (**1**) in the absence of catalyst and/or of light. Furthermore, experiments carried out in the absence of oxygen showed also no evidence of products formed.

All these results confirm the essential role of oxygen, TiO_2, and light in the PCO process. This indicates the predominance of the e^-/h^+ mechanism via the formation of the e^-/h^+ pair at the surface of the Ag/TiO_2 nanoparticles followed by oxidation of the adsorbed 1,2-cyclohexandiol, as indicated in Scheme 1.

KINETIC STUDIES

The semilogarithmic plot of the concentration of 1,2-cyclohexanediol (**1**) at different intervals (Fig. 4) indicates that PCO of **1** can be described by the first-order kinetic model:

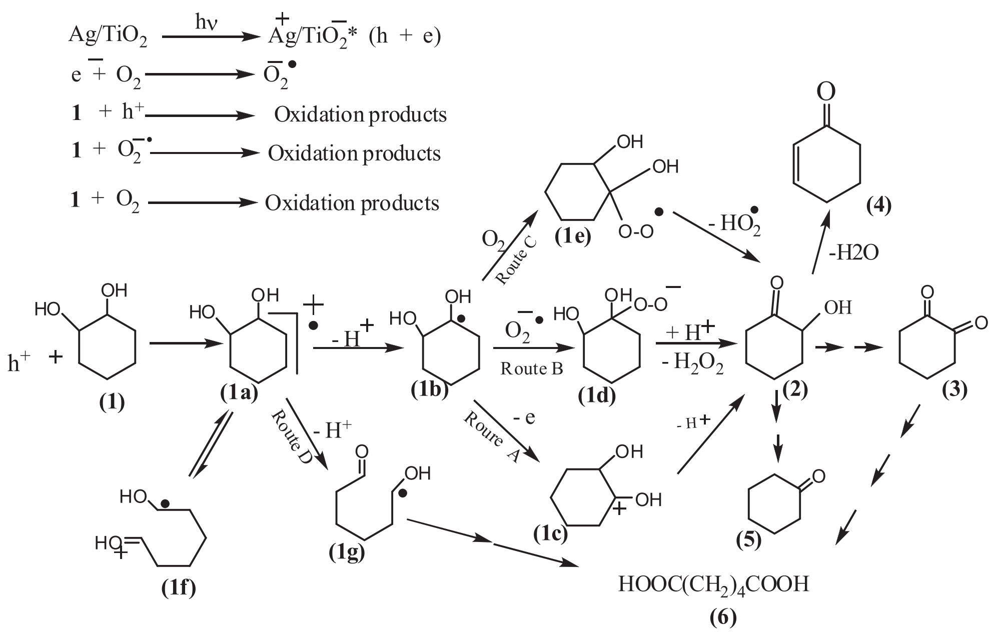
$$\ln C = -kt + \ln C_0$$

where C_0 is the initial concentration, and C is the concentration at time t.

This result is in agreement with the results of Cinar[19] and Liu[30] on PCO m-cresol and phenol, respectively, as well as with our work on cyclohexyl alcohols.[20,21] The rate constant (k) of **1** under the working conditions was found to be equal to -0.145 h^{-1}.

CONCLUSION

Ag/TiO_2 catalyst was prepared in nanoscale size (19–24 nm) and used for PCO of 1,2-cyclohexandiol in the presence of molecular oxygen. The PCO products included 2-hydroxylcyclohexanone (**2**), 1,2-cyclohexanedione (**3**), 2-cyclohexenone (**4**), cyclohexanone (**5**), and adipic acid (**6**). The formation of electron–hole pair at the surface of the semiconductor followed by oxidation



Scheme 1. Photocatalytic oxidation of **1** in acetonitrile

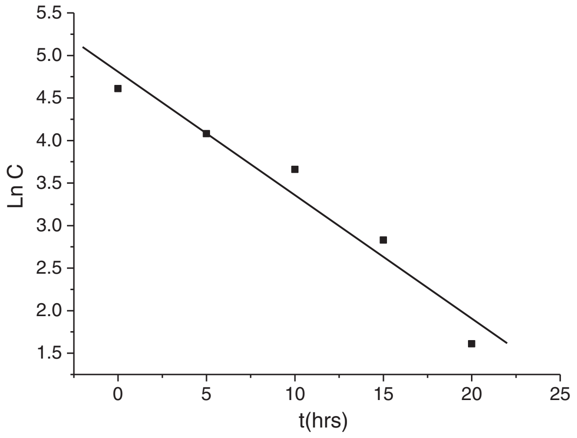


Figure 4. First-order PCO of **1** in acetonitrile ($r = 0.9886$, $k = -0.145\ h^{-1}$)

reactions was the suggested mechanism. PCO of **1** under the applied conditions was found to follow a first-order mechanism with rate constant (k) equal to $-0.145\ h^{-1}$.

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