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Selective photocatalytic oxidation of benzyl alcohol to benzaldehyde by using metal-loaded g-C₃N₄ photocatalysts

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ABSTRACT

Replacement of traditional thermal synthesis of fine chemicals by selective photocatalysis can lead to more environmental friendly processes, carried out at milder conditions, using ambient temperature, atmospheric pressure, with more ecological and economic solvents such as water. Because benzaldehyde (BAL), as fine chemical building block, has an enormous range of applications in pharmaceutical, fragrance and agricultural industries, we analyzed its route of synthesis by the photocatalytic oxidation of benzyl alcohol (BA).

In this work, we used graphitized-carbon nitride (g-C₃N₄) as photocatalyst for the selective synthesis of benzaldehyde from benzyl alcohol. The solid matrix of the photocatalyst was modified by loading different metals such as Au, Ru, Pd, Pt, Ir, Ag and Rh. Conversion, yield and selectivity were compared against benchmark commercial photocatalyst P25 TiO₂ (by Evonik). The influence of the physical-chemical nature of the medium, by means of the pH, on the efficiency of the photocatalytic process was also evaluated. The 1 wt.% Ru/g-C₃N₄ photocatalyst had the best compromise between conversion (73%) and selectivity (72%) for a 4 h of irradiation time using 390 nm activation by a light emitting diode source and it proved to be stable up to 3 consecutive runs.

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1. Introduction

Heterogeneous photocatalytic reactions driven by semiconductor nanomaterials are becoming important for process intensification and safety in many environmental, chemical, pharmaceutical and medical applications [1–3].

Current photo-assisted technologies are mainly based on the use of TiO₂ as photocatalyst due to its chemical stability, inexpensive and low toxicity for humans and environment.

In the domain of semi-conductive carbon materials with photocatalytic activity, the graphitized carbon nitrides, with general formula g-C₃N₄ consisting of C, N and some minor H content, can be synthesized through solvent-free routes starting from nitrogen and carbon rich compounds. They can be prepared by simple low-cost methods at different amount scales tuning its superficial chemistry by simple modification of the preparation process without signif-

icant alteration of the overall composition. Due to its polymeric nature, it is possible to exert control over the surface chemistry via molecular-level modification and surface engineering. This material attracted attention of several authors since can be effectively activated by visible light excitation. Compared to TiO₂, the benchmark photocatalyst, g-C₃N₄ presents a smaller bandgap of 2.7 eV, expanding the absorption from the blue side of the electromagnetic spectrum well in the visible, up to 450 nm (contrasting to the 380 nm absorption edge of TiO₂).

At the present, the use of heterogeneous photocatalysis is mainly concentrated in applications for the treatment of pollutant-contaminated waters [4–7], H₂ production [8–10] and CO₂ reduction [11–13]. More recently, some studies appeared in the domain of selective conversions [14,15]. Selective photo-oxidation can be competitive for photocatalytic fine chemical applications because of its environmentally friendly and energy sustainable characteristics [16]. It was already recognized that besides offering an alternative green route for replacing environmentally hazardous processes, high selectivity could also be achieved by the photocatalytic processes when compared with the conventional methods in

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the case of the synthesis of valuable compounds [17]. Specifically, partial oxidation of alcohols to their corresponding aldehydes and ketones is an important reaction at both bench- and industrial-scale since methanol produced by natural gas, coal and biomass can be used to produce various important and high added-value industrial chemicals [17].

Most of the authors describe the photocatalytic synthesis of benzaldehyde (BAL) from benzyl alcohol (BA) using organic solvents and severe conditions as high temperature or pressure [18–24]. Recent references to the reaction in aqueous media reported a limited conversion of BA and low values of BAL yield and selectivity [25–27]. A study on CdS/g-C₃N₄ composites, reports 45% of BAL yield [28] and g-C₃N₄ modifications by acid treatments results in only 23% of BAL yield [29]. Yet, both studies use organic solvents (benzotrifluoride) and somehow high temperatures and pressures (60–100 °C; 0.5 MPa). Moreover, it is known that CdS can undergo photocorrosion and is reported to be toxic due to the possible release of Cd²⁺ ions in the solution [30].

The present work, is to the best of our knowledge the first example of selective photocatalytic oxidation of BA into BAL in aqueous solution, using g-C₃N₄ materials under mild conditions of ambient temperature and pressure, and an energy-efficient lighting source (UV light emitting diode, LED technology). Noble metals were loaded on the g-C₃N₄ matrix with the aim of increasing the extent and lifetime of the charge separation state. The used noble metals included Au, Ru, Pd, Pt, Ir, Ag and Rh, which efficiency on the performance of the base g-C₃N₄ was compared with the benchmark P25 TiO₂ material from Evonik. A choice of different pH values was used to investigate the influence of this fundamental physical-chemical parameter. Finally, reutilization runs were performed to assay photocatalyst stability.

2. Materials and methods

2.1. Materials

Dicyandiamide (99%, Sigma-Aldrich) was used as precursor for the synthesis of g-C₃N₄. Aeroxide TiO₂ P25 (Evonik) was used as received. The precursors employed for metal impregnation were ruthenium (III) chloride (RuCl₃, 99.9%), rhodium (III) chloride hydrate (RhCl₃·xH₂O, 38.5–45.5%), gold (III) chloride trihydrate (HAuCl₄·3H₂O, 99.99%), silver nitrate (AgNO₃, 99.9%), hydrogen hexachloroiridate (IV) hydrate (H₂Cl₆Ir·xH₂O, 99.9%) and palladium (II) chloride (PdCl₂, 99.9%), all supplied by Alfa Aesar, and dihydrogen hexachloro platinate (IV) hexahydrate (H₂PtCl₆·6H₂O, 99.9%) by Sigma-Aldrich. Sulfuric acid (H₂SO₄, 95–98%, Sigma-Aldrich) and sodium hydroxide (NaOH, 97%, Sigma-Aldrich) were used for pH adjustment. Methanol (CH₃OH, HPLC grade, VWR), sodium hydrogen phosphate (NaH₂PO₄, ≥99.0%, Fluka Analytical), phosphoric acid (H₃PO₄, 85.4%, Fisher Scientific UK) and ultra-pure water (Direct-Q Millipore system) were used for high performance liquid chromatography (HPLC).

2.2. Synthesis of g-C₃N₄ and metal loading

The synthesis of g-C₃N₄ was performed by thermal decomposition of dicyandiamide. Briefly, the precursor was placed in a semi-closed crucible inside a muffle furnace under static air conditions. The equipment was programmed to heat at a 2 °C min⁻¹ ramp up to 450 °C and to maintain that temperature for 2 h, followed by heating up to 550 °C and maintain that temperature for 4 h. The synthesized material was then rinsed with water to remove any unreacted precursor and dried overnight at 100 °C.

Metals were loaded on g-C₃N₄ and on TiO₂ P25 by the incipient wetness impregnation method. Briefly, the photocatalyst was

placed in an Erlenmeyer flask and sonicated for 30 min. Then, an aqueous solution containing the metal precursor (1 wt.% of metal) was pumped into the flask. The material was maintained under sonication for 90 min and then dried at 100 °C for 24 h. Finally, the catalysts were heat treated under nitrogen flow at 200 °C (Au, Pd and Pt) or 350 °C (Ag, Rh, Ru and Ir), for 1 h and reduced at the same temperature under hydrogen flow for 3 h. The calcination/reduction temperatures were selected based on previous temperature programmed reduction (TPR) experiments (not shown).

2.3. Characterization techniques

The materials were analyzed by diffuse reflectance UV–vis spectrometry (DR UV–vis) using a Jasco V-560 apparatus, equipped with an integrating sphere attachment (JASCO ISV-469). DR UV–vis spectra were recorded in diffuse reflectance mode and converted to equivalent absorption Kubelka–Munk units. Fourier transform infrared (FTIR) measurements were performed on a FTIR Nicolet 510-P spectrometer (Thermo Fisher Scientific) equipped with a MIRacle TM Single Reflection ATR (attenuated total reflectance ZnSe crystal plate) accessory (PIKE Technologies). Transmission electron microscopy (TEM) images were obtained using a LEO 906E instrument operating at 120 kV, equipped with a 4 M pixel 28 × 28 mm CCD camera from TRS. X-ray diffraction (XRD) analysis was carried out in a PANalytical X'Pert MPD equipped with a X'Celerator detector and secondary monochromator (Cu Kα λ = 0.154 nm, 40 kV, 30 mA; data recorded at a 0.017° step size, 100 s/step). Elemental analysis was performed using a Carlo Erba EA 1108 instrument.

2.4. Photocatalytic experiments

The reaction setup used for the photocatalytic conversion of BA to BAL consisted in a circular flat glass reactor (5 cm diameter; 1.5 cm thickness; 30 mL total volume), located at 6.5 cm from the irradiation source, which was filled with 28 mL of BA aqueous solution (1.5 mM, initial pH adjusted using H₂SO₄) and 28 mg of catalyst. The system was continuously purged with argon (10 mL min⁻¹) and kept under dark conditions for 15 min. After that period, irradiation was initiated using a UV-LED emitting at 390 nm. Samples were periodically withdrawn for determination of BA and BAL concentration by HPLC-DAD. Light intensity reaching the reactor using UV-LED was 220 W m⁻², determined by using a UV–vis spectroradiometer (OceanOptics USB2000+).

BA conversion (C) and BAL selectivity (S) and yield (Y) were determined as follows:

$$C (\%) = \frac{C_{BA_0} - C_{BA}}{C_{BA_0}} \times 100 \quad (1)$$

$$S (\%) = \frac{C_{BAL}}{C_{BA_0} - C_{BA}} \times 100 \quad (2)$$

$$Y (\%) = \frac{C_{BAL}}{C_{BA_0}} \times 100 \quad (3)$$

where C_{BA0} is the initial concentration (mM) of BA, and C_{BA} and C_{BAL} are the concentrations (mM) of BA and BAL, respectively, at a given time during the photocatalytic reaction.

2.5. Analytical techniques

The concentrations of BA and BAL were determined following HPLC analysis using a Hitachi Elite LaChrom system equipped with a diode array detector (L-2450), a solvent delivery pump (L-2130) and a Purospher Star RP-18 endcapped column (250 mm × 4.6 mm, 5 μm particles). An isocratic method set at a flow rate of

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