FULL PAPER



Preparation of an organic-inorganic hybrid based on synergy of Brønsted and Lewis acid centres as heterogeneous magnetic nanocatalyst for ultrafast synthesis of acetaminophen

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Research Council of Shahid Chamran University of Ahvaz, Iran., Grant/Award Number: 1395 A heterogeneous nanocatalyst based on a Cu(II) complex containing phosphotungstic acid and N/O-donor ligands supported on cobalt ferrite nanoparticles was successfully prepared. The synthesized nanocatalyst was characterized using various techniques. The magnetic nanocatalyst was examined as an efficient and synergistic catalyst for ultrafast synthesis of acetaminophen at room temperature and under solventless conditions. The examined synergistic nanocatalyst, which has both Lewis and Brønsted acidic sites, could be easily separated from the reaction system and reused several times without significant loss of its activity. The synthesized acetaminophen was also fully characterized.

KEYWORDS

acetaminophen, cobalt ferrite, organic-inorganic hybrid, phosphotungstic acid, synergistic catalysis

1 | INTRODUCTION

Polyoxometalates (POMs) include a broad class of transition metal oxide clusters in which the metals (V, Nb, Ta, Mo, W) are usually in their highest oxidation states. Although fundamental studies of these compounds have been carried out in past decades, they are now becoming highly attractive because of their diverse applications in medicine, material science, photochemistry, catalysis, electronics, etc. Due to their acid–base nature and interesting redox properties, POMs have been much used as catalysts in many important organic reactions. Moreover, their acid–base and redox properties can be tuned by simply changing the polyanion chemical composition. Another attractive feature of POMs is that they exhibit gradual multielectron redox process while retaining their well-defined molecular structure.^[1-4]

Among the well-known POM compounds, phosphotungstic acid (PTA), $H_3PW_{12}O_{40}$, has been one of the most studied catalysts. PTA has received much attention in recent years for two main reasons: its strong acidity and ease of preparation. In spite of these advantages of PTA as a catalyst, however, it suffers from some problems, including high solubility in polar solvents and very low surface area in its solid state.^[5–7]

POM clusters have recently been proven to be suitable inorganic ligands for the synthesis and construction of hybrid organic–inorganic materials containing active transition metal coordination complexes and metal–organic building blocks. The central metals of some transition metal complexes can be linked through a POM unit, such as $H_3PW_{12}O_{40}$, to design efficient heterogeneous POM catalysts.^[8–17] Interestingly, the possible emergence of a synergistic effect between the active inorganic (Brønsted acid) and metal–organic (Lewis acid) building blocks can enhance the catalytic efficiency of a designed catalyst. Moreover, combination of a heterogeneous catalyst with a magnetic component will facilitate the recycling process

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of the catalyst. This can be achieved using several methods, the common protocol being to support the catalyst onto a magnetic, stable and inert material to afford a magnetic heterogeneous catalyst.^[18–21]

Magnetic nanoparticles are frequently used as cores in the design of efficient heterogeneous catalysts. Ferrites, a well-known class of magnetic nanoparticles, have the general formula of MFe₂O₄, in which M is a divalent metal. Among these ferrites, cobalt ferrite shows interesting properties, such as high magnetic susceptibility as well as excellent thermal and chemical stability. This ferrite has found potential applications in a variety of fields, one of which is as a support for catalyst immobilization. Therefore, a composite consisting of PTA coordinated to a metal complex supported on cobalt ferrite nanoparticles is expected to be an efficient catalyst because of the presence of two types of acidic sites.^[22–27]

Paracetamol, commonly known as acetaminophen or *N*-acetyl-*p*-aminophenol, is a noteworthy and valuable

nonsteroidal anti-inflammatory drug which was introduced to medicine in 1893. Acetaminophen is produced on a huge scale annually because of its widespread use for the relief of pain and fever in patients with osteoarthritis, simple headaches and non-inflammatory musculoskeletal diseases. In addition to its use as a drug, acetaminophen is also used as a starting material for the synthesis of many important organic compounds. Therefore, the desired synthesis method for acetaminophen must be efficient, simple, safe and cost effective. Due to the growing demand for acetaminophen and high global market value, introducing a new method for improving the presently used synthesis procedure is of great importance. Since the discovery of this drug, several synthesis methods have been explored and reported.[28-31]

In the study reported here, acetaminophen was synthesized from its precursors using a novel magnetic synergistic nanocatalyst consisting of PTA and a Cu(II)



SCHEME 1 Step-by-step synthesis of CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)]

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complex anchored on the surface of cobalt ferrite nanoparticles. The prepared nanocatalyst contains copper metal as Lewis acid, and PTA as Brønsted acid in its molecular structure.

2 | RESULTS AND DISCUSSION

The synthesized nanocatalyst hybrid is designated as $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ and its step-by-step preparation is shown in Scheme 1. Cobalt ferrite (CF) was first functionalized with amine groups and then salicylaldehyde (SA) was added to give CF@Si-N=SA. PTA, 2,2'-bipyridine (bipy) and copper(II) sulfate were subsequently added to the latter composite to obtain the final $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ hybrid. According to the results of various analyses, a structure was proposed for the synthesized nanocatalyst which is shown in Scheme 1.

2.1 | Fourier transform infrared (FT-IR) spectroscopy

For characterization of all the prepared compounds, FT-IR spectroscopy was used. The FT-IR spectrum of CF (Figure 1a) shows two main peaks at 420 and 588 cm^{-1} related to Fe-O stretching at the tetrahedral and octahedral sites, respectively. The FT-IR spectrum of CF@Si-NH₂ is presented in Figure 1(b) which shows some bands related to the symmetric vibration modes of Si-O-Si bonds, in addition to the peaks observed for CF. After linking of SA with the amine-functionalized CF, the observed FT-IR spectrum (Figure 1c) shows bands at 1196–1626 cm^{-1} ascribed to C=N in the Si-N=SA moiety. The FT-IR spectrum of the final CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] nanocatalyst (Figure 1d) contains a band at 1114 cm⁻¹ related to the stretching of Si—O bond, a characteristic band at 977 cm⁻¹ attributed to $\nu(W-O_t)$, a band at 883 cm⁻¹ ascribed to $\nu(WO_{\rm b}-W)$ and another peak at 815 cm⁻¹ due to



FIGURE 1 FT-IR spectra of (a) CoFe₂O₄, (b) CF@Si-NH₂, (c) CF@Si—N=SA, (d) CF@[Cu₂(Si—N=SA) ₂(bipy)₂(PTA)] and (e) PTA ν (W—O_c). The peak at 1080 cm⁻¹ corresponding to asymmetric vibration of P—O in the tetrahedral PO₄ of pure PTA (Figure 1e) is overlapping with the peaks of the organic ligands in CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] composite and cannot be clearly seen. However, two distinct peaks at 988 and 891 cm⁻¹ for the free PTA have an apparent red shift and are seen at 977 and 883 cm⁻¹, respectively. This shift to low frequency can be due to the coordination of PTA to copper metal which increases their force constants. This observation confirms the presence of PTA as coordinated ligand to the copper metal in the as-synthesized composite.

2.2 | Powder X-ray diffraction (PXRD) analysis

The crystalline natures of the as-synthesized products were characterized using PXRD analysis and the PXRD patterns are presented in Figure 2. In the PXRD pattern of $CoFe_2O_4$ (Figure 2, blue) strong peaks are observed which belong to the Bragg reflection planes of (220), (311), (400), (422), (511) and (440) for $CoFe_2O_4$ (JCPDS card no. 22–1086). When the copper complex is wrapped on the surface of CF, the same PXRD peaks of the ferrite are seen but with less intensity. The appearance of a strong peak at $2\theta = 17^{\circ}$ in the PXRD pattern of

CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] (Figure 2, black) can be attributed to the presence of the copper complex in this hybrid because this peak can be seen in the PXRD pattern of the unsupported copper complex (Figure 2, orange). The sharp peaks observed in the PXRD pattern of pure PTA (Figure 2, green) cannot be easily seen in the pattern of CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] probably because of the destruction of its crystal structure after immobilization. The crystallite size of free CoFe₂O₄ nanoparticles was about 18 nm and their sizes were found to be 30 nm in the final nanocatatlyst, as measured using the well-known Debye–Scherrer formula.^[32]

2.3 | Thermogravimetric analysis (TGA)

The TGA curve of $[Cu_2(Si - N = SA)_2(bipy)_2(PTA)]$ (Figure 3a) can be divided into four stages. The first stage is from room temperature to 120 °C with a weight loss of 1.1%, consistent with the release of the crystallization water molecules in this hybrid. The second stage is from 120 to 340 °C with a weight loss of 6%, which is due to the release of the organic ligand in $[Cu_2(Si - N = SA)_2(bipy)_2(PTA)]$. The third stage is from 340 to 450 °C with a weight loss of 18.2%, which corresponds to the combustion of residual organic ligands. In the ultimate step, a weight loss of 5% from 450 to 1000 °C is related to complete decomposition



FIGURE 2 PXRD patterns of CoFe₂O₄ (blue), CF@[Cu₂(Si—N=SA)₂(bipy)₂ (PTA)] (black), [Cu₂(Si—N=SA)₂(bipy)₂ (PTA)] (orange) and PTA (green)



FIGURE 3 TGA thermograms of (a) [Cu₂(Si—N=SA)₂(bipy)₂(PTA)] and (b) CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)]

of the $[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ composite. The total weight of volatile material in the TGA curve for $[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ is 30.3%. The TGA curve of CF@ $[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ nanocatalyst shown in Figure 3(b) is more or less the same as that of the inorganic–organic hybrid complex, with the only difference being 4% greater weight loss. This additional weight loss for the nanocatalyst can be due to the release of water molecules from CF magnetic core.

2.4 | Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis

The morphology of $CoFe_2O_4$ and $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ was determined using SEM and TEM techniques. SEM images of $CoFe_2O_4$ and nanocatalyst are depicted in Figure 4. In both these samples the particles have almost spherical morphology. The TEM image of CF nanoparticles also shows spherical morphology for this ferrite. The nanocatalyst appears as a



 $\label{eq:FIGURE 4} \begin{array}{ll} (a, b) \mbox{ SEM and } (c, d) \mbox{ TEM images of } (a, c) \mbox{ CoFe}_2O_4 \\ \mbox{ and } (b, d) \mbox{ CF}@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)] \end{array}$

chain-like structure in the TEM image (Figure 4d) due to its polymeric nature resulting through the formation of copper complex on the surface of CF.

The elemental composition of the as-synthesized $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ was determined using EDX analysis and the EDX spectrum is depicted in Figure 5. Distinct peaks are seen related to W, Cu, Fe, Co, Si, P, C, O and N elements. The EDX results for the nanocatalyst indicate a mixture of two phases, i.e. CF and organic–inorganic hybrid complex. The EDX results can prove the presence of CF and organic–inorganic hybrid complex in the nanocatalyst.

2.5 | Magnetic properties

Magnetization measurements of the as-synthesized nanocatalyst, as well as of bare CF, were performed using a vibrating sample magnetometer at room temperature with an applied magnetic field of 10 kOe. The hysteresis loops of these magnetic nanoparticles are displayed in Figure 6. The saturation magnetization (M_s) of the pristine CF (61.5 emu g⁻¹) is markedly reduced to 8.3 emu g⁻¹ on functionalization with the copper inorganic–organic complex hybrid. The decrease in M_s for the final nanocatalyst can be due to the share of non-magnetic components on the surface of magnetic CoFe₂O₄ core. In spite of the significant decrease of M_s for the nanocatalyst, its net magnetism is still sufficiently high for effective recovery and separation of the catalyst from a reaction mixture via applying an external magnetic field.

2.6 | Brunauer-Emmett-teller analysis

Surface area, pore volume and pore size distribution of CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] were determined through Brunauer–Emmett–Teller and Barrett–Joyner–

Halenda methods from the adsorption of nitrogen at 77 K using a Micrometrics Gemini analyser. Nitrogen adsorption–desorption and pore size distributions isotherms of the nanocatalyst are shown in Figure 7. The hysteresis curves demonstrate a type II isotherm for the nanocatalyst. The mean pore diameter, pore volume and surface areas of CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] are 17.80 nm, 0.07 cm³ g⁻¹ and 16.40 m² g⁻¹, respectively.

2.7 | Catalytic study

The characterization of the prepared acetaminophen, as well as determination of its yield, was achieved using GC analysis. The physical and FT-IR spectral data of the obtained acetaminophen were compared with those reported in the literature. Melting point: 170 °C. FT-IR (KBr): $\nu_{\rm N-H} = 3325$ cm⁻¹, $\nu_{\rm OH} = 3170$ cm⁻¹, $\nu_{\rm C=O} = 1666$ cm⁻¹ (Figure S1).

The acetaminophen product, which was obtained from the reaction of *p*-hydroxyaniline with acetic anhydride catalysed by the as-prepared nanocatalyst, was also characterized using elemental analysis (CHN), ¹H NMR and GC–MS techniques. Anal. Calcd for C₈H₉NO₂ (%): C, 63.5; H, 6.00; N, 9.26. Found (%): C, 63.10; H, 6.01; N, 9.31. ¹H NMR (CDCl₃, 250 MHz, δ , ppm): 10.2 (s, 1H, NH), 9.4 (s, 1H, OH), 6.5 (d, 2H, ArH), 7.5 (d, 2H, ArH), 2.1 (s, 3H, CH₃) (Figure S2). GC–MS analysis presented an EI-MS spectrum with intense molecular ion peak (M⁺, *m/z* 151.3) (Figure S3).

The PXRD pattern of acetaminophen depends on many factors, one of which is the recrystallization conditions. Thus, acetaminophen has different crystal structures and each of these structures has its specific PXRD pattern.^[32–36] The PXRD pattern of the synthesized acetaminophen was recorded in the range of Bragg angles $2\theta = 10-80^{\circ}$ and is presented in Figure S4. The sharpness



FIGURE 5 EDX spectrum of CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)]



FIGURE 6 Hysteresis loops of (a) $CoFe_2O_4$ and (b) $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$

of the observed peaks indicates that the prepared acetaminophen is highly crystalline and is of high purity. The PXRD pattern of acetaminophen showed several peaks at 18°, 20°, 37.5°, 47.5° and 79°.

Due to the simultaneous presence of two active catalytic sites in this catalyst, it can act as a highly efficient catalyst for the instant synthesis of acetaminophen under very mild conditions. The reaction for the synthesis of acetaminophen was examined with pure PTA and Cu(II) salt separately and it was found that neither of these two materials gave satisfactory product yield even at higher temperature and longer reaction time. Therefore, each of Cu(II) as Lewis acid and PTA as Brønsted acid exhibited poor performance in catalysing the synthesis of acetaminophen. However, when these two are combined in a single catalyst, the catalytic efficiency is enhanced markedly.

Stability and reusability of a nanocatalyst are of great importance and must be evaluated for any heterogeneous catalysts. Therefore, after completion of the reaction, the catalyst was isolated from the reaction medium with the aid of an external magnet and used in a subsequent reaction. The results in Table 1 show



FIGURE 7 Nitrogen adsorption-desorption and pore size distributions isotherms of CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)]

 TABLE 1
 Reusability of CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)]

 nanocatalyst

Run	Fresh	1	2	3	4	5
Yield (%)	98	98	98	96	94	93

that an excellent yield of acetaminophen (above 93%) is obtained even for the fifth run. The Cu content of the $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ nanocatalyst after the fourth run was 6.58%. Based on these findings, the loss of Cu content of the catalyst after four successive runs was only 0.3%. The observed results reveal that the $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ nanocatalyst

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has high stability with negligible leaching. Therefore, this catalyst can be considered as a green and efficient catalyst for the synthesis of acetaminophen and similar compounds. In a preliminary study, the same reaction for the preparation of acetaminophen was examined using aniline, instead of *p*-aminophenol, in the presence of the as-synthesized catalyst, and was shown to be a promising method for the synthesis of acetanilide product. Therefore, it is expected that other acetanilide derivatives can be synthesized using this procedure.

3 | CONCLUSIONS

Briefly, an organic-inorganic hybrid Cu(II) complex containing mixed N/O donor ligands and PTA supported on CF nanoparticles has been prepared. The as-prepared nanocatalyst hybrid was investigated as a green and magnetically recoverable catalyst for ultrafast synthesis of acetaminophen under very mild conditions. The most prominent features of the catalytic system include: (1) solvent-free conditions or the use of nontoxic solvents such as ethanol, (2) efficient magnetic recovery of the nanocatalyst, (3) the possible occurrence of a synergistic effect between the Lewis and Brønsted acidic active sites and (4) ultrafast and facile synthesis of pure acetaminophen. This catalytic system, therefore, can be considered as a green, efficient and cost-effective one for the synthesis of acetaminophen.

4 | EXPERIMENTAL

4.1 | General

All the chemicals used in this study were of reagent grade and were used without further purification. FT-IR spectra were recorded as KBr pellets with a PerkinElmer Spectrum One spectrophotometer. PXRD patterns of the synthesized samples were obtained with a Philips X-ray diffractometer (model PW1840) over a 2θ range from 10° to 80° using Cu K α radiation ($\lambda = 1.54056$ Å). SEM images were obtained using an S4160 (Hitachi, Japan) scanning electron microscope. The magnetic properties of the fabricated CF@Si@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] nanocatalyst as well as other samples were studied using a vibrating sample magnetometer (Meghnatis Daghigh Kavir Company). The content copper of the nanocatalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Horiba Jobin Yvon, Longjumeau, France). Reaction yields were determined with GC-FID (Agilent Technologies, 7890A).

4.2 | Synthesis of CF@Si@[Cu₂(Si—N=SA) ₂(bipy)₂(PTA)]

CF magnetic nanoparticles were synthesized according to a procedure reported in the literature.^[37] Amine functionalization of CF was successfully achieved as follows. An amount of 1.0 g of CoFe₂O₄ was dispersed in a mixture of 5 ml of deionized water and 20 ml of absolute ethanol. To this suspension, 0.4 ml of ammonia (25%) and 0.5 ml of (3-aminopropyl)triethoxysilane (APTES) were added. The reaction mixture was stirred for 3 h at room temperature to ensure hydrolysis of APTES and functionalization of CF surface with amine groups. The amine-functionalized CF (CF@Si-NH₂) was separated by magnetic decantation, washed with ethanol and dried in an oven at 100 °C for 2 h. In the next step, 0.5 g of the as-prepared CF@Si-NH₂ was added to a solution of SA (0.37 g) in ethanol (15 ml) and the mixture was refluxed for 24 h. The product was separated magnetically, washed with distilled water and dried at 60 °C to give CF@Si-N=SA as a black powder. Finally, to a magnetically stirred suspension of CF@Si-N=SA (0.5 g) in ethanol (20 ml), a solution containing CuSO₄·6H₂O (0.5 g, 2 mmol), PTA (0.1 g, 0.05 mmol) and 2,2'-bipyridine (0.08 g, 0.5 mmol) in deionized water (10 ml) was added and the whole was refluxed for 24 h. The obtained final product, as black solid, was separated from the solution by applying an external magnetic field and washed with deionized water. After drying in an oven at 100 °C for 24 h, the CF@[Cu₂(Si—N=SA)₂(bipy)₂(PTA)] nanocatalyst was afforded.^[10,11] Based on ICP-AES analysis, the content of copper of the nanocatalyst was 6.6%.

4.3 | Synthesis of acetaminophen in presence of as-prepared catalyst

For the ultrafast synthesis of acetaminophen, 0.015 g of $CF@[Cu_2(Si-N=SA)_2(bipy)_2(PTA)]$ nanocatalyst was added to a mixture of p-hydroxyaniline (2 mmol) and acetic anhydride (2 mmol) and the neat mixture was stirred at room temperature for 1 min. After that, the reaction mixture became completely solid. The extraction of the product was achieved by addition of water (5 ml) to the obtained solid. The nanocatalyst was separated using a permanent magnet, dried and reused for another reaction run under the same conditions. The remaining aqueous solution, which contained the acetaminophen product, was left for gradual evaporation of the solvent under air to afford the crude acetaminophen product. The product was purified by recrystallization from hot water to give white brilliant crystals of acetaminophen with high yield (98%) and purity (Figure S5).

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SUPPORTING INFORMATION

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