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Synthesis of Fe$_2$O$_3$ Nanoparticles and their Catalytic Activity for the Reduction of Halonitroarenes under Sustainable Conditions

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Fe$_2$O$_3$ nanoparticles (NPs) with mean size of 50 nm ca. are synthesized starting from a porous organic polymer containing β-ketoesterate Fe(III) sites (Fe-POP), which is annealed at 400 °C under air for 30 min. During calcination, the organic material partially decomposes, and iron(III) oxide NPs onto an organic residue could be observed after annealing. The obtained NPs are characterized by SEM-EDS, IR, and magnetic analyses and they are employed as active catalysts in the reduction of *p*-bromonitrobenzene into *p*-bromoaniline, using hydrazine hydrate in ethanol.

1. Introduction

The catalytic reduction of nitroarenes toward anilines is an important reaction from both academic and industrial points of view, being the resulting products important intermediates to produce dyes, agrochemicals, pigments, and pharmaceuticals.[1] In addition, removal of nitroarene pollutants from water by reducing them into anilines is a valuable method to purify contaminated matrices. Such reductive reactions are frequently carried out by using noble metal catalysts,[2] which are usually very active and recyclable in some cases. Recently, the use of earth abundant metal catalysts has raised great interest especially for economic reasons, as these materials are generally cheap and easy to be reached.[3] In this framework, iron oxide catalysts are very attractive because they are not expensive and not toxic. Herein, we report on the synthesis of Fe$_2$O$_3$ nanoparticles (NPs) with a mean size of 50 nm ca. obtained by annealing a polymer supported β-ketoesterate Fe(III) complex (Fe-POP) at 400 °C under air for 30 min, thus proposing a novel method of iron oxide preparation.[4] The obtained NPs were characterized by Scanning Electron Microscopy – Energy Dispersive Spectrometry (SEM-EDS), Infrared (IR) spectroscopy, and magnetic analyses and were employed as active and selective catalyst in the reduction of *p*-bromo-nitrobenzene into *p*-bromo-aniline, using hydrazine hydrate in ethanol.

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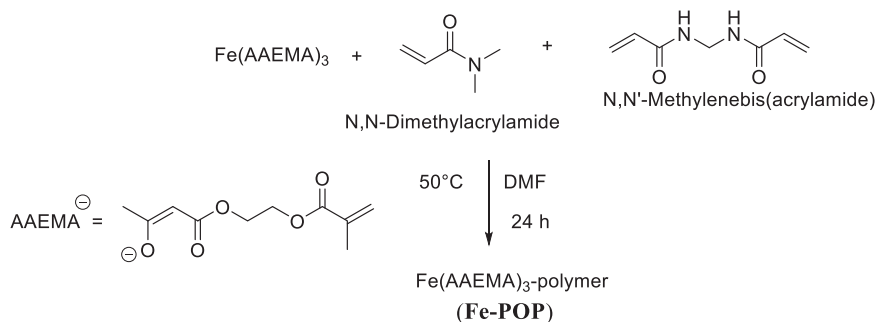via Orabona, Bari 4 – 70125, Italy
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2. Results and Discussion

The synthesis of the acrylamidic porous organic polymer Fe-POP, supporting β-ketoesterate Fe(III) centers homogeneously dispersed throughout the matrix occurred by copolymerization of the metal containing monomer Fe(AAEMA)$_3$ with suitable comonomer and cross-linker, as summarized in **Scheme 1**.

Fe-POP was annealed under air at 400 °C for 30 min. During this process, the material lost almost quantitatively its polymer matrix and gave rise to a red powder (RP), identified as Fe$_2$O$_3$ NPs supported onto an organic residue (**Scheme 2**).

SEM micrographs of RP showed its nanometric structure composed by spheric nanoparticles whose diameter ranged from 22 to 80 nm, with a mean value of 50 nm ca. (**Figure 1**). EDS spectra revealed the massive presence of iron and oxygen in the chemical composition of the obtained NPs together with a small amount of carbon and the absence of nitrogen (**Figure 2**). EDS elemental analyses quantified an iron content of 58%$_w$.

IR spectrum of RP (**Figure 3**) showed two strong Fe—O peaks at 457 and 534 cm^{-1} tentatively ascribable to hematite iron oxide,[5] along with an intense broad band between 1606 and 1300 cm^{-1} due to overlapping signals of various organic functionalities

Fe(AAEMA)₃ + N,N-Dimethylacrylamide + N,N'-Methylenebis(acrylamide)

$$\xrightarrow[\text{24 h}]{\text{50°C} \mid \text{DMF}}$$

Fe(AAEMA)₃-polymer
(Fe-POP)

Scheme 1. Synthesis of Fe-POP.

Fe-POP $\xrightarrow[\text{400°C, 30 min}]{\text{calcination under air}}$ red powder RP (Fe₂O₃ NPs)

Scheme 2. Synthesis of Fe₂O₃ NPs.

(C = O, C = C, etc.), not well defined due to sintering and pyrolysis processes, occurred during calcination.

The magnetic behavior of RP was studied by recording the magnetization curve at 300 K (**Figure 4**), which suggested the presence of magnetic impurities, considering that M value of bulk hematite is 0.4 emu g^{-1}. However, further investigations (X-ray diffraction and Raman spectroscopy) are required to check the exact nature of the iron oxide phases.

All described analyses strongly indicated that RP was constituted by Fe₂O₃ nanoparticles supported onto a small amount of organic residue, coming from the combustion of the pristine polymeric support. The catalytic activity of RP (Fe₂O₃ NPs) was tested in the selective reduction of *p*-bromonitrobenzene, using hydrazine hydrate as the reductant[6] (**Scheme 3**).

Preliminary experiments showed that the catalytic system was able to convert 40% of the initial amount of the substrate in 2 h reaction and it was selective toward the formation of *p*-bromoaniline without producing hydro-dehalogenation side products.
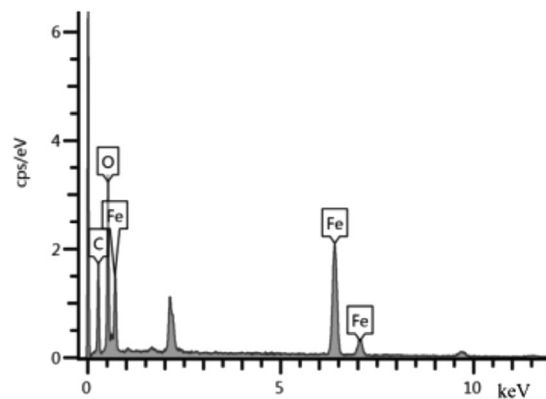

Figure 2. EDS spectrum of RP. EDS indicates energy dispersive spectrometer; RP, red powder.

3. Conclusion

The synthesis of iron oxide nanoparticles onto an organic residue (RP) was achieved by heating a polymer supported *β*-ketoesterate
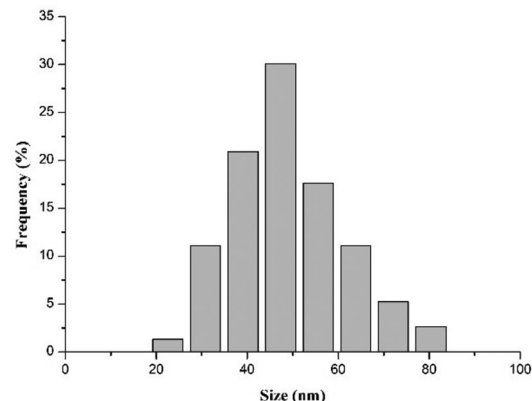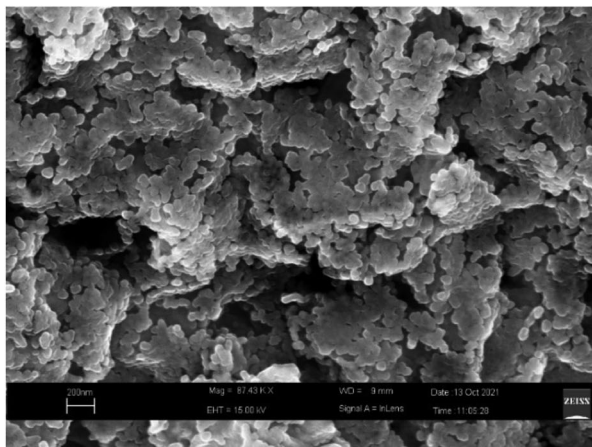

Figure 1. SEM micrograph (left) and size distribution nanoparticles (right) of the calcined sample (RP). RP indicates red powder; SEM, Scanning Electron Microscopy.
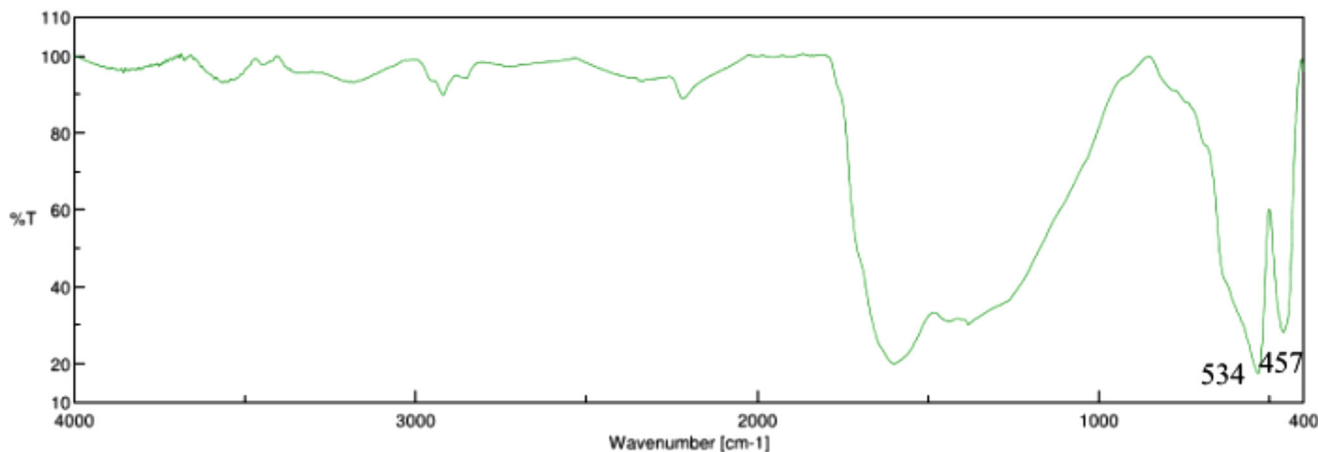
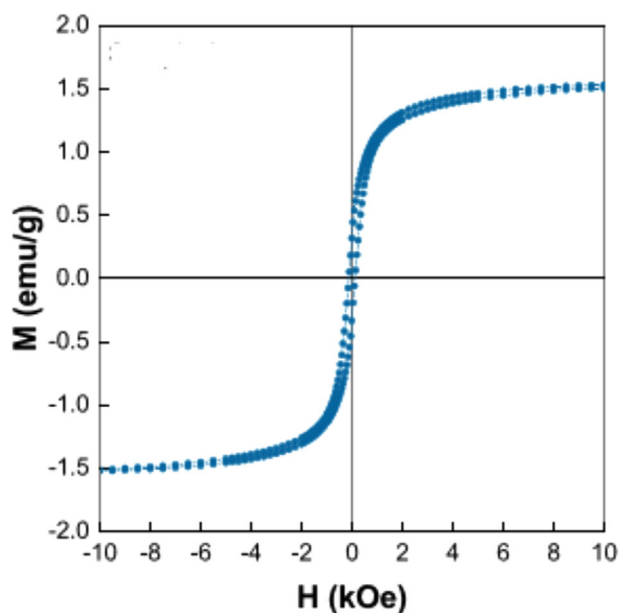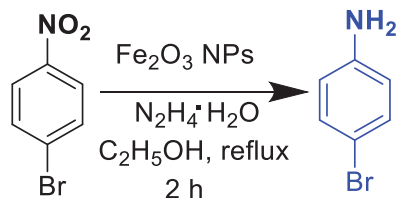**Figure 3.** IR spectrum of RP (KBr). IR indicates infrared; RP, red powder.

Figure 4. M versus H curve at 300 K for RP. RP indicates red powder.

conversion = 40%, selectivity > 99%

Scheme 3. Catalytic activity of RP in the reduction of *p*-bromonitrobenzene. RP indicates red powder; SEM, Scanning Electron Microscopy.

iron(III) complex under air at 400 °C for 30 min. SEM, EDS, and IR spectroscopic techniques along with magnetic measurements were used to characterize the phase, the morphology, the size, and the magnetism of the obtained product, which seemed composed mainly of nano-hematite. The mean particle diameter of the nanoparticles was equal to 50 nm ca., while their size ranged from 22 to 80 nm. Preliminary catalytic tests showed that RP was an active and selective catalyst for the reduction of *p*-bromonitrobenzene into *p*-bromoaniline, using hydrazine hydrate as the reductant.

4. Experimental Section

Materials and Methods: Tap water was de-ionized by ionic exchange resins (Millipore) before use. All other chemicals were purchased from commercial sources and used as received. $Fe(AAEMA)_3$ [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethylmethacrylate] was synthesized according to literature procedure.[7] Reactions were monitored by gas–liquid chromatography (GLC) analyses. GLC analysis of the products was performed using a HP 6890 instrument equipped with a FID detector and a HP-1 (Crosslinked Methyl Siloxane) capillary column (60.0 m × 0.25 mm × 1.0 μm). The products were identified by comparison of their retention times with those of reference materials. Morphological analyses were performed with a scanning electron microscope (SEM) Zeiss Σigma 300 VP (Zeiss Oberkochen, Germany) equipped with an energy dispersive spectrometer (EDS) C-MaxN SDD with an active area of 20 mm^2 (Oxford Instruments, Oxford, UK). Iron content was assessed by EDS measurements, after deposition of very dilute sample dispersions in water on aluminum stubs. The particle sizes were analyzed by SEM image analysis using the ImageJ software (freeware software: http://rsb.info.nih.gov/ij/). FT-IR spectra (in KBr pellets) were recorded on a Jasco FT/IR 4200 spectrophotometer. Field dependent magnetic measurements were carried out at 300 K using a vibrating sample magnetometer (MicroSense, model 10).

Synthesis of Fe-POP: $Fe(AAEMA)_3$ (1.7 mmol, 1.2 g) [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethylmethacrylate] was dissolved in *N,N*-dimethylformamide (DMF, 3.5 mL) and the resulting solution was added of a mixture of *N,N'*-methylenebisacrylamide (1.1 mmol, 0.17 g) and N,N-dimethylacrylamide (30.3 mmol, 3.0 g) in DMF (3.5 mL) and heated at 50 °C under vigorous stirring for 24 h. The orange jelly polymer was filtered off, washed with acetone (3 × 10 mL) and diethyl ether (3 × 10 mL), and dried under vacuum. Yield = 4.2 g of polymer (Fe-POP). Elemental analysis (found): Fe 2.40%$_w$.

Synthesis of Fe_2O_3 NPs (here Referred as RP): Fe-POP (1.4 g) was annealed under air and kept at the final temperature of 400 °C for 30 min, yielding a red powder (RP). Yield = 80 mg. Elemental analysis Fe 58%$_w$.

Catalytic Tests: 0.50 mmol of *p*-bromonitrobenzene and the catalyst (9.0 mg of RP containing 0.047 mmol of Fe_2O_3) were placed in a 25 mL

flask. Then, 2.0 mmoL of $N_2H_4 \cdot H_2O$ and 5 mL of ethanol were added, and the resulting mixture was put at 80 °C in an oil bath and left under stirring for 2 h under refluxing conditions. The progress of the reaction was monitored by GLC. Conversions and yields were calculated by using biphenyl as internal standard.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

[1] G. Romanazzi, V. Petrelli, A. M. Fiore, P. Mastrorilli, M. M. Dell'Anna, *Molecules* **2021**, *26*, 1120.

[2] M. M. Dell'Anna, S. Intini, G. Romanazzi, A. Rizzuti, C. Leonelli, F. Piccinni, P. Mastrorilli, *J. Mol. Catal. A: Chem.* **2014**, *395*, 307.

[3] G. Romanazzi, A. M. Fiore, M. Mali, A. Rizzuti, C. Leonelli, A. Nacci, P. Mastrorilli, M. M. Dell'Anna, *Mol. Catal.* **2018**, *446*, 31.

[4] N. Ajinkya, X. Yu, P. Kaithal, H. Luo, P. Somani, S. Ramakrishna, *Materials* **2020**, *13*, 4644.

[5] U. Schweitmann, R. M. Cornell, "*Iron Oxides in the Laboratory, Preparation and Characterization*", Wiley-VCH, Weinheim, **2008**.

[6] J. Lv, Z. Liu, Z. Dong, *Mol. Catal.* **2020**, *498*, 111249.

[7] P. Mastrorilli, C. F. Nobile, G. Marchese, *Inorganica Chim. Acta* **1995**, *233*, 65.