

Magnetically Recyclable Nanocatalysts: Eco-friendly Solutions for Green Catalysis

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ABSTRACT

In the last decades, there has been an escalating concern about environmental protection, which motivated the quest for novel cost-effective sustainable catalytic technologies. With the advent of Nanoscience, magnetic nanomaterials such as transition metal nanoferrites, conquered new horizons in Green Catalysis. By combining the intrinsic advantages of nanosize materials with the easy recovery by magnetic separation, magnetic nanoparticles unlocked the gateway to a new generation of recyclable nanocatalysts.

This work provides an overview of our recent breakthroughs in the design of magnetically recyclable nanocatalysts. We will start by presenting their application as *catalyst supports* for the immobilization of (a) a metal complex with high catalytic efficiency in oxidation reactions and (b) gold nanoparticles catalytically active in the 4-nitrophenol reduction. In a distinct approach, superparamagnetic nanoferrites were used as *intrinsic catalysts* in the degradation of a dye.

Keywords: magnetic nanoparticles; nanocatalysis; geraniol epoxidation; 4-nitrophenol reduction; dye degradation

1 INTRODUCTION

Catalysis is a keystone technology in the Chemical and Petrochemical Industry, being applied in more than 90% of the chemical processes worldwide. In the last decades, the global concern for environmental protection boosted the development of more sustainable and cost-effective catalytic processes [1]. The advances in Nanoscience and Nanotechnology revolutionized the area of Green Catalysis, paving the way to a new generation of eco-friendly recyclable nanocatalysts [1].

In particular, magnetic nanoparticles (MNPs) such as iron oxides and spinel-type transition metal ferrites (MFe_2O_4 , where M(II) is a *d*-block transition metal) conquered new horizons in this field, either as intrinsic catalysts or as catalyst supports – the so-called hybrid nanocatalysts [1]. Their nanometer size, high surface area to volume ratio and easy dispersion in several solvents are some of their remarkable features [2]. Additionally, their magnetic properties allow the efficient recovery from the reaction medium by magnetic separation, thus providing a greener route for catalyst recycling.

In order to improve the chemical stability and dispersion of the MNPs in the reaction medium, some catalytic

reactions require their coating with protective shells (silica, carbon, polymer). Silica coatings are of particular interest since they enable the easy surface modification, offering the possibility of introducing new functionalities onto the nanoparticles surface.

In this work we will provide an overview of our recent breakthroughs in the design of magnetically recyclable nanocatalysts, using superparamagnetic nanomaterials either as catalyst supports or as intrinsic catalysts.

Amine-functionalized silica-coated maghemite (γ - Fe_2O_3) nanoparticles were used as support for the immobilization of a metal complex, oxidovanadium(IV) acetylacetone ([VO(acac)₂]), with high catalytic efficiency in the epoxidation of allylic alcohols [3]. The novel magnetic hybrid nanomaterial was tested in the epoxidation of geraniol and its catalytic performance was compared with that of the homogeneous counterpart and of other bulk and nanocatalysts reported in literature.

More recently, mesoporous silica-coated $MnFe_2O_4$ MNPs functionalized with amine and thiol groups were used as supports for gold nanoparticles (Au NPs). The resulting hybrid nanocatalysts were evaluated in the reduction of 4-nitrophenol (4-NP).

Finally, a novel generation of superparamagnetic MFe_2O_4 ($M = Co(II), Fe(II), Mn(II)$) nanoferrites with decreased particle size and enhanced saturation magnetization [4] were applied as nanocatalysts in the degradation of methylene blue dye through the Fenton reaction.

2 EXPERIMENTAL

2.1 Preparation of Hybrid [VO(acac)₂] Magnetic Nanocatalyst

The [VO(acac)₂] hybrid magnetic nanocatalyst was prepared in a multi-step procedure reported in [3]: (i) preparation of γ - Fe_2O_3 MNPs by coprecipitation, (ii) coating of the magnetic cores with two silica shells with different thicknesses using sodium silicate (first layer) and tetraethylorthosilicate (TEOS; second layer) as silica precursors, (iii) functionalization of the silica-coated MNPs with 3-aminopropyltriethoxysilane (APTES), (iv) immobilization of [VO(acac)₂] onto the amine-functionalized magnetic nanosupport. The resulting nanomaterial will be denoted as γ - $Fe_2O_3@SiO_2-NH_2-V$.

2.2 Preparation of Nanogold Hybrid Catalyst

Superparamagnetic MnFe_2O_4 nanoparticles were prepared as described in section 2.3 (see below). Afterwards, the magnetic nanomaterial was firstly coated with a thin and non-porous silica layer, followed by the coating with a mesoporous silica layer and simultaneous functionalization with APTES or 3-mercaptopropyltrimethoxysilane (MPTMS) by co-condensation. Finally, the Au NPs were immobilized onto the resulting nanomaterials by *in situ* reduction of $[\text{AuCl}_4]$ using citric acid as reducing agent [5]. The resulting nanocatalysts will be denoted as $\text{MnFe}_2\text{O}_4@\text{SiO}_2@m\text{SiO}_2-\text{X}@\text{Au}$, where X = NH₂ or SH.

2.3 Preparation of Superparamagnetic MFe_2O_4 (M=Co, Fe, Mn) Nanocatalysts

The superparamagnetic MFe_2O_4 (M = Co(II), Fe(II), Mn(II)) nanocatalysts were prepared by a novel coprecipitation route recently developed by our group, using isopropanolamine as alkaline agent and water as solvent. A detailed description of the experimental procedure is reported in reference 4.

2.4 Catalytic Experiments

2.4.1 Epoxidation of geraniol

The geraniol epoxidation was carried out at room temperature using 1.00 mmol of geraniol (substrate), 0.50 mmol of chlorobenzene (GC internal standard), 1.50 mmol of *tert*-butyl hydroperoxide and 0.050 g of $[\text{VO}(\text{acac})_2]$ magnetic nanocatalyst in 5.00 cm³ of dichloromethane, under stirring conditions [3]. The progress of the reaction was monitored by gas chromatography.

2.4.2 Reduction of 4-nitrophenol

The $\text{MnFe}_2\text{O}_4@\text{SiO}_2@m\text{SiO}_2-\text{X}@\text{Au}$ (0.030 g) nanocatalysts were tested in the reduction of 4-NP, at room temperature in water, in the presence of NaBH₄ reducing agent. The reaction progress was monitored by UV-Vis spectroscopy. The experimental procedure was adapted from reference 6.

2.4.3 Degradation of methylene blue dye

The MFe_2O_4 nanocatalysts (1.2 g L⁻¹) were tested in the degradation of methylene blue (50 mg L⁻¹), at room temperature in water and neutral pH, in the presence of H₂O₂ (10.5 mol L⁻¹). The reaction progress was monitored by UV-Vis spectroscopy. Furthermore, at the end of the reaction and after the catalyst separation, the reaction mixtures were analyzed by ¹H NMR.

3 RESULTS AND DISCUSSION

3.1 Magnetic $[\text{VO}(\text{acac})_2]$ Hybrid Nanocatalyst for the Epoxidation of Geraniol

Vanadium complexes are very efficient homogeneous catalysts in liquid-phase epoxidation reactions, for the production of epoxides, which are valuable building blocks for the synthesis of natural products and biologically active compounds [7]. In particular, $[\text{VO}(\text{acac})_2]$, has been reported as a highly active, regio- and stereoselective catalyst in the epoxidation of allylic alcohols to the corresponding epoxyalcohols. Despite these advantages, the low chemical and thermal stabilities and difficult separation from the reaction medium inherent to homogeneous catalysts are major drawbacks towards the principles of Green Chemistry, preventing their application in Industry [1]. The immobilization of metal complexes onto solid supports constitutes a potential strategy to overcome these limitations, leading to the development of more sustainable catalytic processes.

$[\text{VO}(\text{acac})_2]$ was anchored onto superparamagnetic γ -Fe₂O₃ nanoparticles coated with silica and functionalized with amine groups [3]. The silica-coated MNPs presented an average particle size of ~240 nm particle, with ~6.5 nm γ -Fe₂O₃ cores, as revealed by electron microscopy (Fig. 1).



Figure 1: Epoxidation of geraniol catalyzed by γ -Fe₂O₃@SiO₂-NH₂-V magnetic nanocatalyst.

The results from chemical analysis and XPS confirmed the efficient immobilization of $[\text{VO}(\text{acac})_2]$ on the surface of the silica-coated MNPs functionalized with amine groups, leading to a vanadium bulk content (by chemical analysis) of 35 $\mu\text{mol g}^{-1}$. Additionally, the binding energies of N 1s (400.2 eV) and V 2p_{3/2} (516.9 eV) obtained by XPS presented a slight shift relative to those of the nanosupport (400.0 eV) and free complex (517.1 eV), respectively; these results, in combination with previous work concerning $[\text{M}(\text{acac})_2]$ (M = Cu(II) and VO(IV)) immobilization onto amine-functionalized materials, suggested the covalent bonding of the complex to the nanosupport through the amine groups [8].

The novel hybrid magnetic nanocatalyst was tested in the epoxidation of geraniol, at room temperature in

dichloromethane, using *tert*-butyl hydroperoxide as oxidant (Fig. 1). The nanocatalyst led to 100% geraniol conversion and 96% selectivity towards 2,3-epoxygeraniol, being comparable to the values achieved under homogeneous conditions. More remarkably, when compared with $[VO(acac)_2]$ -based heterogeneous bulk catalysts, it led to a reduction of the reaction time from 48 to 30 h with the additional advantage of magnetic separation, albeit its smaller complex loading ($35 \mu\text{mol g}^{-1}$ vs. $86\text{--}137 \mu\text{mol g}^{-1}$). The improved performance of the hybrid nanocatalyst was assigned to the nanosize of the support which enhanced the dispersion of the catalytic active sites in the reaction medium, overcoming the diffusion limitations typical of heterogeneous catalysts.

More recently, we were able to reach a significantly lower reaction time, through the covalent grafting of the complex onto $\sim 45 \text{ nm}$ non-magnetic amine-functionalized silica nanoparticles [8]. The resulting hybrid nanocatalyst reached 100% of substrate conversion and 99% of 2,3-epoxygeraniol selectivity after only 2 h and preserved its catalytic efficiency upon reuse in further four cycles. The reduction of the support dimensions to sizes below 100 nm played a determinant role on these achievements, being responsible not only for the improved catalytic performance but also for the immobilization of a higher amount of complex ($295 \mu\text{mol g}^{-1}$).

3.2 Nanogold Hybrid Catalyst for the Reduction of 4-Nitrophenol

Gold nanoparticles play an important role as nanocatalysts for the degradation of organic pollutants; in particular, they are efficient catalysts for the low temperature reduction of 4-NP, which is used in the production of pesticides and dyes and commonly found in the resulting wastewaters [9]. However, since Au NPs aggregate very easily, they are generally immobilized onto solid supports.

In this work mesoporous silica-coated superparamagnetic MnFe_2O_4 nanoparticles functionalized with amine or thiol groups, with average particle size of $\sim 175 \pm 20 \text{ nm}$ (9.3 nm magnetic cores), were used as support for the *in situ* immobilization of Au NPs ($4.4 \pm 1.1 \text{ nm}$; Fig. 2). The effect of the type of organosilane linker (APTES or MPTMS) on the *in situ* immobilization of the Au NPs was evaluated. The XPS results confirmed the efficient grafting of the Au NPs on both supports through the amine and thiol groups. However, the $\text{MnFe}_2\text{O}_4@\text{SiO}_2@m\text{SiO}_2-\text{SH}@\text{Au}$ hybrid nanocatalyst presented a significantly higher Au surface content than $\text{MnFe}_2\text{O}_4@\text{SiO}_2@m\text{SiO}_2-\text{NH}_2@ \text{Au}$, 0.3 vs. 0.03%, highlighting the importance of thiol groups as tethering agents.

Both hybrid nanocatalysts were tested in the reduction of 4-NP to 4-aminophenol, in water in the presence of NaBH_4 , presenting 100% conversion after $\sim 15 \text{ min}$, albeit the different Au loading (Fig. 2). Furthermore, the

nanocatalysts were stable upon reuse in four further cycles, preserving their catalytic performance with negligible Au leaching.

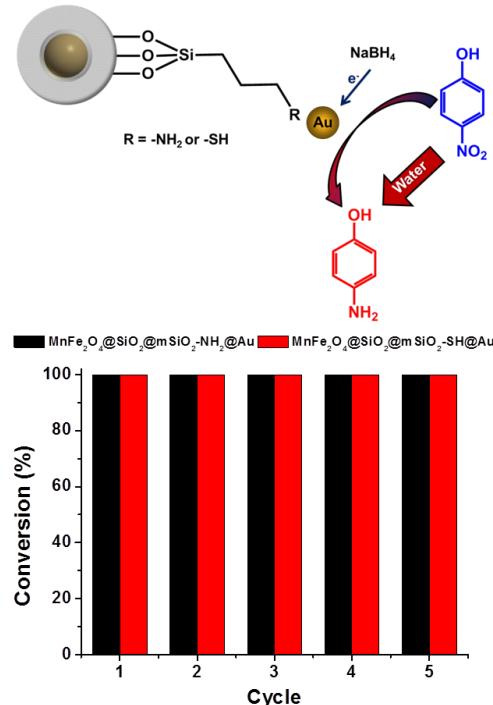


Figure 2: 4-Nitrophenol reduction catalyzed by nanogold anchored onto functionalized silica-coated MnFe_2O_4 MNPs.

3.3 MFe_2O_4 Nanoferrites as Fenton Catalysts for Dye Degradation

Over the year, the global concern with the environmental protection has lead to the development of novel and more efficient wastewater treatment technologies. The Fenton process is among the most economically viable wastewater treatments for the degradation of organic pollutants and dyes [10]. Recently, heterogeneous catalytic systems attracted huge interest since the catalyst can be recycled and the process works at neutral pH. MNPs, such as spinel-type nanoferrites (MFe_2O_4 , where $\text{M} = d$ -block transition metal) open promising perspectives in this field.

A novel generation of water-dispersible MFe_2O_4 superparamagnetic nanocatalysts with reduced particle size (4.8, 6.3 and 9.1 nm for CoFe_2O_4 , Fe_3O_4 and MnFe_2O_4 , respectively, by XRD) and enhanced saturation magnetization has been recently produced by our group through a novel coprecipitation route [4].

The superparamagnetic nanomaterials were tested as intrinsic nanocatalysts in the degradation of methylene blue dye through the Fenton reaction (neutral pH, Fig. 3). All catalysts presented medium to high activity in the dye degradation, with efficiencies of 41, 62 and 84% for Fe_3O_4 , MnFe_2O_4 and CoFe_2O_4 , respectively, after 24 h. CoFe_2O_4 , with the smallest particle size, was the most efficient.

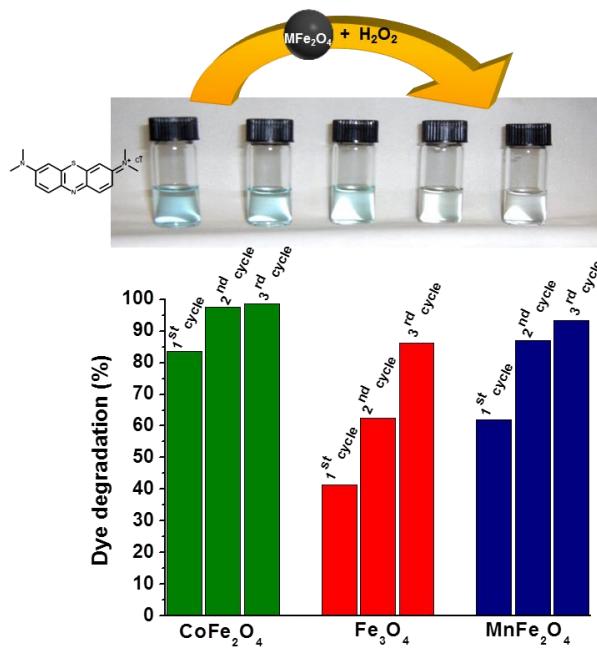


Figure 3: Degradation of methylene blue dye catalyzed by superparamagnetic MFe₂O₄ nanoparticles.

More remarkably, the nanocatalysts were stable upon reuse in two cycles, reaching higher degradation efficiencies (86–99% after 3 cycles) in the same reaction time. After the catalytic cycles, infrared spectroscopy (not shown) and XRD studies (Fig. 4) were performed. Both techniques revealed that the structure and particle size of the magnetic nanoferrites were preserved, confirming their chemical stability upon reuse.

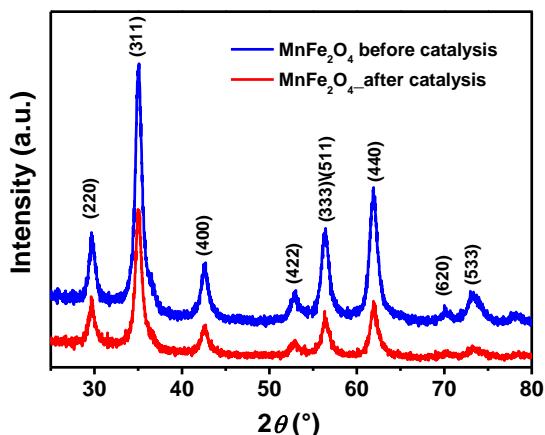


Figure 4: X-ray diffractograms of MnFe₂O₄ before and after the catalytic experiments.

4 CONCLUSIONS

Superparamagnetic iron oxides and transition metal nanoferrites were designed for the production of eco-friendly magnetically recyclable nanocatalysts.

Silica-coated MNPs were successfully used as supports for the immobilization of two types of catalysts: the transition metal complex [VO(acac)₂] which is a highly active catalyst for epoxidation reactions, and gold nanoparticles which have an important role as catalysts for the degradation of organic pollutants. The resulting hybrid nanocatalysts presented high catalytic performances, with the additional advantage of easy recovery by magnetic separation. Superparamagnetic nanoferrites were also efficient intrinsic nanocatalysts for dye degradation.

In conclusion, magnetically recyclable nanocatalysts represent a step forward in the design of new eco-friendly solutions for a more sustainable Chemistry, blurring the boundaries between homogeneous and heterogeneous catalysis. In the near future we will probably witness a remarkable increase in the number of catalytic technologies based on magnetic nanomaterials.

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