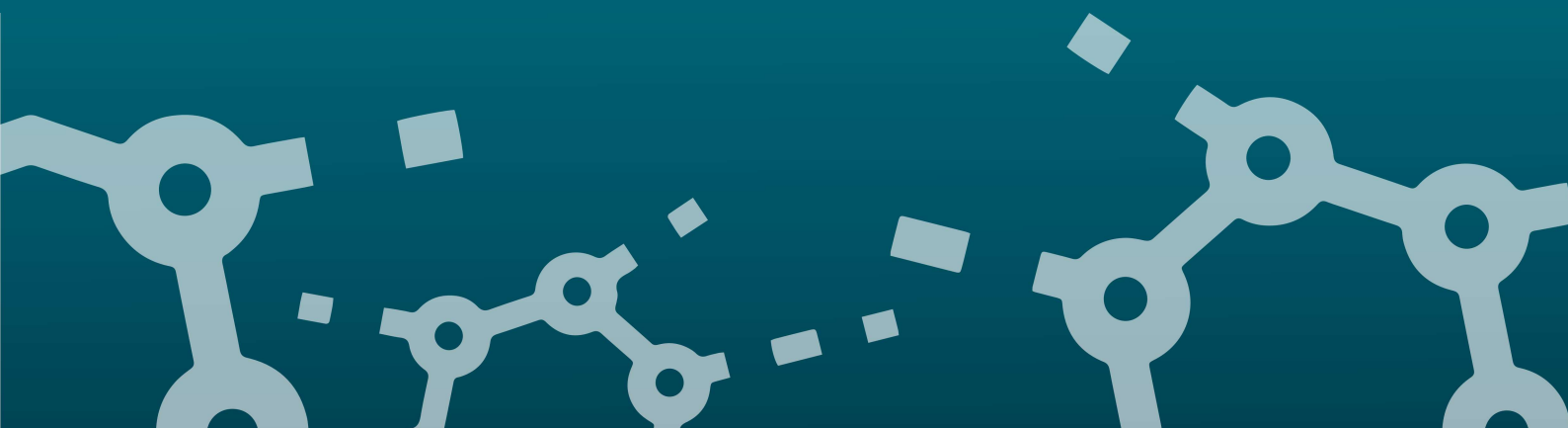


XII CONGRESSO NAZIONALE



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# Catalytic activity of $\text{Fe}_3\text{O}_4/\text{CeO}_2$ nanocomposites prepared by a microwave assisted solvothermal method: imine formation from benzyl alcohol and aniline

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## Introduction

In catalysis, nanocerium has been used as efficient catalyst for aerobic oxidation reactions due to its oxygen storage capability [1], although its recovery at the end of the catalytic cycle cannot be carried out by simple filtration, because of its too tiny texture [2]. A method to overcome this disadvantage is to cover magnetite ( $\text{Fe}_3\text{O}_4$ ) with nanocerium [3], in order to remove the whole material easily from the reaction mixture by using an external magnet. The focus of this contribution is to verify, whether: i) the nanocerium deposition process changes the pristine morphology of the magnetite nanoparticles, ii) the different morphologies of magnetite seeds synthesized using various organic stabilizer (polyvinylpyrrolidone, trisodium citrate dihydrate or oleic acid) during the preparation of the catalyst can influence its catalytic activity in the imine formation from benzyl alcohol and aniline.

## Materials and methods

Magnetite nanoparticles with different morphologies were prepared by a hydrothermal synthesis assisted by microwave irradiation using  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  as precursor and hydrated hydrazine in alkaline condition as oxidant agent, as reported in ref. [4]. For microwave assisted solvothermal syntheses an ETHOS E-TOUCH Milestone applicator was used.

### *Synthesis of $\text{Fe}_3\text{O}_4/\text{CeO}_2$ nanocomposites*

In a typical reaction,  $\text{Fe}_3\text{O}_4$  (0.1000 g, 0.432 mmol) and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  (0.3534 g, 0.645 mmol, Ce/ $\text{Fe}_3\text{O}_4$  molar ratio = 1.5) were mixed in ethylene glycol (15 mL) in a 100-mL Teflon® autoclave. The microwave power was adjusted to reach the settled temperature of 200°C in 10 min with a dwell time of 45 min. After reaction, the vessel was cooled down to room temperature by means of ventilation applied to the vessels inside the microwave applicator. After the work-up of the as-obtained dark suspension a black powder was finally obtained.

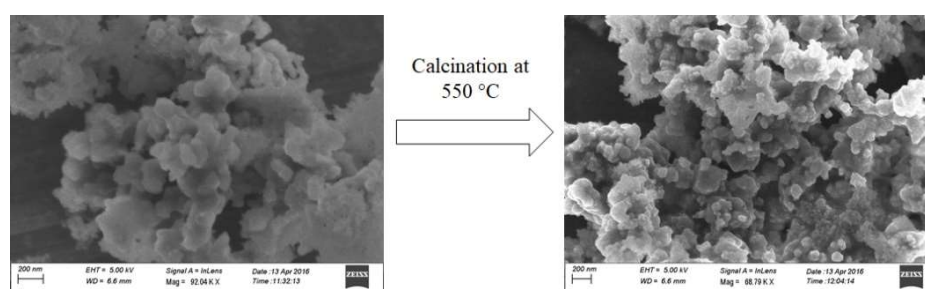
### *Catalytic experiments*

Benzyl alcohol (21.6 mg, 0.2 mmol) and aniline (37.3 mg, 0.4 mmol) were put in a glass tube under air without solvent. Then, the appropriate amount of catalyst was added and stirred vigorously at 50°C for 3h. Afterwards, the reaction mixture was cooled to room temperature and added diphenyl as internal standard and ethanol. The catalyst was clamped with the help of an external magnet and the liquid solution was transferred to a new vial. The catalyst was then washed with ethanol and the washing liquors were collected and added to the reaction

solution for GLC analyses. The catalyst removed from the reaction solution was dried in oven at 80°C overnight and then calcinated at 400°C for 1 h under air, before being used for a subsequent catalytic run.

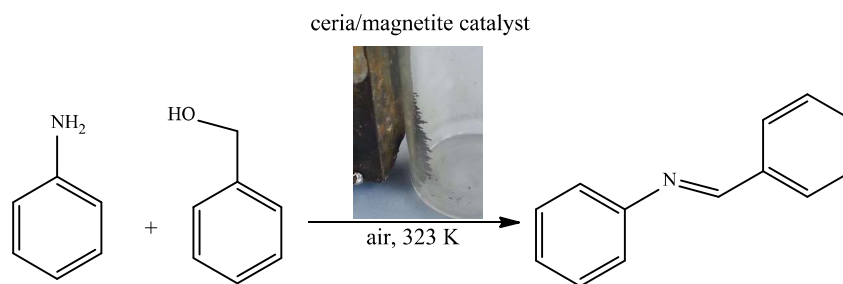
## Results and discussion

A microwave assisted solvothermal procedure in ethylene glycol is proposed to prepare magnetite/ceria nanocomposites by depositing nanoceria on magnetite seeds of different morphologies (hexagonal, spheroidal, quasi-spherical). Results obtained by IR, XRD, FE-SEM and TGA/DSC analyses suggest: i) to calcinate the new materials at 550°C (Figure 1) for avoiding sintering processes and promoting the ceria transition phase from amorphous to crystalline state; and ii) to use at least 1.5 Ce/Fe<sub>3</sub>O<sub>4</sub> molar ratio during preparation for obtaining a more stable magnetite/ceria nanostructure.



**Figure 1.** Change of morphology of Fe<sub>3</sub>O<sub>4</sub>/1.5CeO<sub>2</sub> over a calcination at 550°C.

All nanocomposites resulted magnetically active. The synthesized nanomaterials were tested as catalysts for imine formation from benzyl alcohol and aniline in the absence of any solvent under air (Scheme1). The highest imine conversion rate was obtained with Fe<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub>, prepared in the absence of any organic stabilizer.



**Scheme 1.** Imine synthesis from benzyl alcohol and aniline.

The new catalyst was recyclable for at least five runs. Its catalytic activity increased with the reuses probably because the organic impurities coming from the solvothermal synthesis depleted over the runs, rendering the whole system highly interesting in the field of nano-catalysis.

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