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Cite this: *RSC Adv.*, 2015, 5, 15035

# Gold nanoparticles supported on magnesium ferrite and magnesium oxide for the selective oxidation of benzyl alcohol

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Au nanoparticles (Au NPs) have gained significant attention as catalysts for the selective oxidation of alcohols; however, the catalytic activity is highly dependent on the presence of a base. Alternatives to the use of strong bases, such as NaOH, are still needed. Here, we explored the basicity of magnesium ferrite/oxide supports to study the catalytic behaviour of supported Au NPs for the oxidation of benzyl alcohol. The presence of Mg<sup>2+</sup> ions in the ferrite structure improved the catalytic activity of supported Au NPs to ca. 35% conversion in the absence of an additional base. After modifying the support with MgO, the catalytic activity of supported Au NPs was further improved to ca. 50% conversion, but the catalyst deactivated in successive recycling tests. When the catalysts were tested in the presence of a sub-stoichiometric amount of K<sub>2</sub>CO<sub>3</sub>, they became more active and remained stable upon recycling with no loss of activity and selectivity for the preferential production of benzoic acid.

Received 11th December 2014

Accepted 23rd January 2015

DOI: 10.1039/c4ra16159a

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## Introduction

Benzyl alcohol is a very common substrate used to study selective oxidations catalysed by heterogeneous gold-based catalysts.<sup>1</sup> As a model reaction, it is relatively uncomplicated and allows fundamental studies like the effect of different preparation methods, catalyst supports, metal-support interactions and the need for a base to promote the reaction at reasonable conversion rates. Although the use of benzyl alcohol as a probe is motivated by its simplicity, the importance of its oxidation products is of great relevance to industry. Usually, the goal is the production of the partially oxidized product benzaldehyde, and further oxidation to carboxylic acid is considered less important.<sup>2</sup> Indeed, the partial oxidation product of benzyl alcohol is an industrially very important compound due to its distinctive pleasant, bitter, almond-like scent, which enables it to be employed to manufacture odorants and flavours for food and drinks as well as confer fragrance to perfumes and cosmetics. Beyond that, benzaldehyde is a primary precursor of the synthesis of other organic compounds as plastic additives, dyes and agricultural chemicals.<sup>3</sup> However, the production of benzoic acid by the complete oxidation of the benzyl alcohol

shares an immense importance in industry as well. Benzoic acid is mainly consumed for the production of phenol, and other usages come from the market demands in different countries, as precursors of plasticisers, antiseptics, decongestants and food preservatives, used on its own in a diluted aqueous solution.<sup>4</sup> The fully oxidised product can be as important as the partially oxidised one, if selectively obtained. None of the two compounds are synthesised industrially using gold catalysts.

Gold catalysts studied in the oxidation of benzyl alcohol under certain conditions (usually in the presence of a base) produce benzaldehyde and by-products such as benzylbenzoate<sup>5</sup> and, in some cases, benzoic acid.<sup>6</sup> Less common by-products may also be formed, usually in lower quantities, like benzene and toluene.<sup>7</sup> Higher selectivity to benzaldehyde (and elevated activities) is obtained with bimetallic Au catalysts containing Pd, Pt and Cu<sup>6,8-10</sup> among others and/or employing bases as promoters for solvent-free oxidations.<sup>11,12</sup> The role of metal promoters in the oxidative process is not completely understood; however, the presence of the base may be considered important for the dehydrogenation of the substrate.<sup>1</sup> Beyond the choice of the metallic system (mono or bimetallic) as well as the addition or not of a base, the catalyst support is a third parameter that must be taken into account.

The interaction between the Au catalyst and its support appears to have a huge influence on the selectivity of the system, with little effect of the substrate structure.<sup>13</sup> The influence of the support depends on its composition (CeO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, charcoal, among others), the interfacial connection between the catalyst and the support, the metal loading and the nanoparticle size distribution.<sup>14</sup> The choice of basic solids as catalyst support

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is an attempt to avoid the addition of a base to the reaction mixture. Au NPs supported on  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$  have been explored in oxidation reactions without the need of additional base.<sup>15</sup> There are also examples of metal free catalysts, such as carbon dioxide promoted mesoporous carbon nitride, which can perform oxidation of alcohols using molecular oxygen without base addition.<sup>16</sup>

In continuation of our prior studies in the field of magnetic separation applied to catalysis,<sup>17</sup> where we have mainly used magnetite as a catalyst support, we explored here an attempt to improve the basicity of a still magnetic support by replacing the  $\text{Fe}^{2+}$  ions in the ferrite structure of magnetite by the more alkaline  $\text{Mg}^{2+}$  ions. In this context, we report the preparation of Au NPs supported on basic and magnetic supports and their significant promotional effect on the oxidation of benzyl alcohol.

## Experimental section

### Preparation of $\text{MgFe}_2\text{O}_4$ and $\text{MgO/MgFe}_2\text{O}_4$

Magnesium ferrite nanoparticles ( $\text{MgFe}_2\text{O}_4$ ) were prepared by the co-precipitation method. An aqueous solution of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (5 mL,  $0.84 \text{ mol L}^{-1}$ ) was mixed with an aqueous solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (10 mL,  $0.84 \text{ mol L}^{-1}$ ). The solution containing the metal chlorides was added to 250 mL of ammonium hydroxide solution ( $0.7 \text{ mol L}^{-1}$ , deoxygenated water) under vigorous mechanical stirring (10 000 rpm, Ultra-Turrax T18 Homogenizer, IKA Works) in a nitrogen atmosphere. A gelatinous orange precipitate was immediately formed. After 2 h of stirring, the precipitate was collected with a permanent magnet and the clear supernatant removed. The solid was washed with hot distilled water ( $2 \times 200 \text{ mL}$ ,  $80 \text{ }^\circ\text{C}$ ) and acetone (100 mL), and it subsequently was dried in an oven at  $80 \text{ }^\circ\text{C}$ . The solid was calcined in a muffle furnace in atmospheric air at  $800 \text{ }^\circ\text{C}$  for 4 h, at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

A composite of magnesium oxide/magnesium ferrite ( $\text{MgO/MgFe}_2\text{O}_4$ ) was prepared by an impregnation method.<sup>18</sup>  $\text{MgFe}_2\text{O}_4$  and  $\text{MgO}$  were mixed in a mass ration of 1 : 5 under stirring in aqueous solution and, subsequently, dried in an oven at  $105 \text{ }^\circ\text{C}$  for 24 h. Finally, the dried material was calcined in a muffle furnace in atmospheric air at  $800 \text{ }^\circ\text{C}$  for 4 h, at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

### Synthesis of Au NPs

The gold NPs were prepared by using a method described elsewhere.<sup>19</sup> In a typical procedure, 1.80 mL of an aqueous solution of polyvinyl alcohol 2.0 wt% (PVA, 36 mg) was added under intense magnetic stirring to an aqueous solution of  $\text{HAuCl}_4$  (172.5 mg, 300 mL). The metal reduction occurred after the drop-by-drop addition of 7.65 mL of a freshly prepared aqueous solution of  $\text{NaBH}_4$  ( $0.1 \text{ mol L}^{-1}$ ) under magnetic stirring. The solution turned a dark purple colour, and the system was stirred for 30 additional minutes.

### Immobilisation of pre-formed colloidal NPs

The catalyst support (500 mg) was added to the solution of colloidal Au NPs, prepared as described above. The mixture was stirred at  $25 \text{ }^\circ\text{C}$  for 2 h, after which the solid was magnetically collected from the solution and washed with  $70 \text{ }^\circ\text{C}$ -distilled water ( $2 \times 25 \text{ mL}$ ) and ethanol ( $2 \times 25 \text{ mL}$ ). The final dark brown solid was then dried in atmospheric air at  $80 \text{ }^\circ\text{C}$  for 8 h.

### Catalytic experiments

The oxidation reactions were performed using a 100 mL Fischer–Porter glass reactor. In a typical solventless reaction, the glass reactor was loaded with the supported Au-catalyst (4.1  $\mu\text{mol}$  of Au) and benzyl alcohol (9.6 mmol). The reactor, immersed in an oil bath, was loaded with 2 atm of  $\text{O}_2$ . The temperature was maintained by the oil bath placed on a hot stirring plate connected to a digital controller (ETS-D5 IKA). The reactions were conducted under magnetic stirring, using a Teflon-coated magnetic stir bar, for the desired time. The catalyst was magnetically recovered by placing a permanent magnet on the reactor wall. The products were then collected using a syringe and analysed by gas chromatography (GC) using *p*-xylene as the standard. The isolated catalyst could be reused when a new amount of substrate was added.

### Characterisation

The morphology of the samples was investigated using a Philips CM 200 Transmission Electron Microscope (TEM) operated at 200 kV. For TEM analysis, the samples were prepared by dispersing a few milligrams in acetone at room temperature followed by ultrasonication. One or two drops were further deposited on a 400 mesh carbon-coated Cu grid. The gold content, in all catalysts, was measured by Flame Atomic Absorption Spectroscopy (FAAS) using an Atomic Absorption Spectrophotometer Shimadzu AA-6300. X-ray diffraction (XRD) of the samples was recorded using a Rigaku miniflex diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at a  $2\theta$  range from 10 to  $90$  with a  $0.02^\circ$  step size and measuring time of 5 s per step. The crystal structure and identification of the crystal phases of the samples were performed by Rietveld profile refinement using the Fullprof software.<sup>20</sup> Magnetisation as a function of the applied magnetic field,  $M(H)$  measurements were performed on a PPMS (Physical Property Measurement System) Dynacool from Quantum Design. The samples were cooled to a desired temperature under a zero external magnetic field. After the temperature was established,  $H$  was cycled from 9 to  $-9 \text{ T}$ , back and forth. For any further  $M$  versus  $H$  measurement, the residual magnetic field was reduced near to zero.

## Results and discussion

The magnesium ferrite ( $\text{MgFe}_2\text{O}_4$ ) used as support for gold nanoparticles (Au NPs) was synthesised following the procedure described elsewhere,<sup>21</sup> except for the choice of a different divalent metal ion than iron. The replacement of the  $\text{Fe}^{2+}$  ions in the ferrite structure of magnetite by the more alkaline  $\text{Mg}^{2+}$  ions was an attempt to enhance the basicity of the support. The

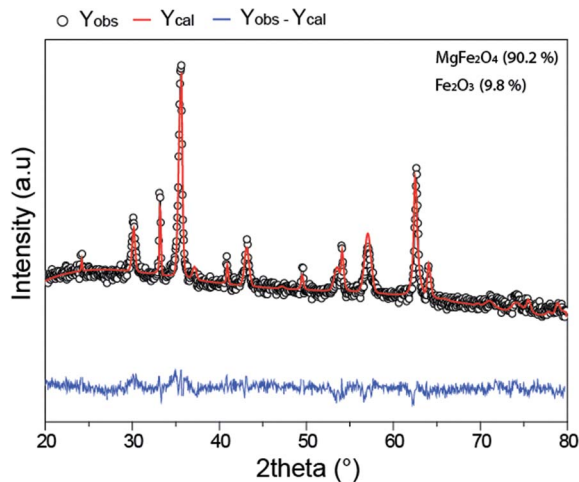


Fig. 1 X-ray diffraction patterns of  $\text{MgFe}_2\text{O}_4$  after calcination at  $800\text{ }^\circ\text{C}$ .

crystal structure of  $\text{MgFe}_2\text{O}_4$  is similar to magnetite ( $\text{Fe}_3\text{O}_4$ ), where  $\text{Fe}^{2+}$  ions are replaced by  $\text{Mg}^{2+}$ . Fig. 1 displays the XRD pattern of the  $\text{MgFe}_2\text{O}_4$  obtained after calcination at  $800\text{ }^\circ\text{C}$  for 4 h (before calcination, the solid was amorphous). The diffraction pattern was indexed to two crystalline phases:  $\text{MgFe}_2\text{O}_4$  (JCPDS PDF #89-1935) and another corresponding to  $\text{Fe}_2\text{O}_3$  (JCPDS PDF #33-0664). The data were refined by using the Rietveld method to quantify the amount of crystalline phases of magnesium ferrite. The Rietveld refinement results indicate that the majority phase is  $\text{MgFe}_2\text{O}_4$  (90.2%); 9.8% remained as non-substitute ferrites ( $\text{Fe}_2\text{O}_3$ ). The refined unit cell parameters for the  $\text{MgFe}_2\text{O}_4$  phase, with space group  $Fd3m$ , were found to be  $a = b = c = 8.39\text{ \AA}$ , values in excellent agreement with those found in the bulk magnesium ferrite (JCPDS PDF #89-1935). We have also found that the average grain size of  $\text{MgFe}_2\text{O}_4$  is about 21.2 nm, and the grains have a preferred orientation along the [311] direction.

The magnesium ferrite,  $\text{MgFe}_2\text{O}_4$ , is an important n-type semiconductor with its crystal structure designated as an inverse spinel structure, which is comprised of a cubic close-packed oxide with one octahedral and two tetrahedral sites per oxide, these being smaller than the others. In this inverse

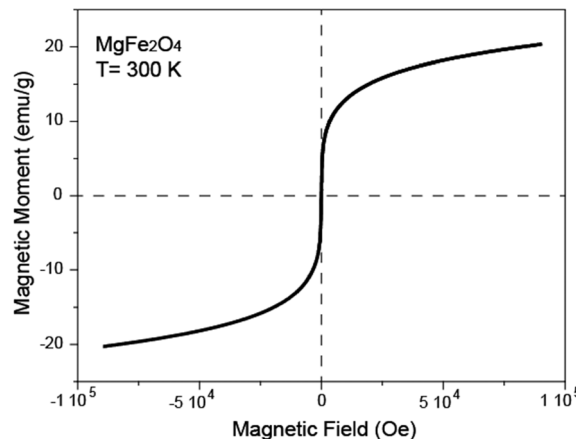


Fig. 2 Temperature dependence of the magnetisation under applied magnetic field of the catalyst support  $\text{MgFe}_2\text{O}_4$  at  $300\text{ K}$ . The hysteresis loops were recorded between  $-9\text{ T}$  and  $9\text{ T}$ .

spinel crystal structure, the cations with valence  $2+$  occupy the octahedral sites, and the cations with valence  $3+$  occupy half the octahedral and half the tetrahedral sites. The main purpose of exchanging  $\text{Fe}^{2+}$  for  $\text{Mg}^{2+}$  ions in this study was to take advantage of the alkalinity of this cation, but it also improved the uptake of gold from the colloidal solution used in the impregnation step.

Impregnation tests performed initially with  $\text{Fe}_3\text{O}_4$  revealed a very poor uptake of PVA-stabilised Au NPs from aqueous colloidal solutions (0.07 wt% Au in the isolated solid). The immobilisation of Au NPs on magnetite is possible, usually, by functionalising the support<sup>11,22</sup> or by slowly adding gold(III) salt, promoting the  $\text{Au}^{3+}$  adsorption before the gold reduction using glucose, borohydride and hydroxylamine, among others.<sup>23,24</sup> Nevertheless, in this study, when the support was modified using  $\text{Mg}^{2+}$ , a one hour impregnation procedure allowed the uptake of 2 wt% metal. Beyond this advantage, the synthesised support was found to exhibit superparamagnetic behaviour at room temperature, according to its magnetic properties displayed in Fig. 2. The catalyst support has the exceptional advantage of being recovered due to its magnetic properties. The material does not exhibit any coercive field or hysteresis at room temperature, which

Table 1 Oxidation reaction of benzyl alcohol using  $\text{Au}/\text{MgFe}_2\text{O}_4$ <sup>a</sup>

Entry	Catalyst	Base added	Conversion (%)	Selectivity (%)	
				Benzaldehyde	Benzoic acid
1	$\text{MgFe}_2\text{O}_4$	—	0	—	—
2	$\text{Au}/\text{MgFe}_2\text{O}_4$	—	35	59	41
3	$\text{Au}/\text{MgFe}_2\text{O}_4$	$\text{K}_2\text{CO}_3$	62	36	64
4	$\text{Au}/\text{MgFe}_2\text{O}_4$	KOH	32	66	34
5	$\text{MgFe}_2\text{O}_4$ <sup>b</sup>	—	0	—	—
6	$\text{Au}/\text{MgFe}_2\text{O}_4$ <sup>b</sup>	—	24	94	6
7	$\text{Au}/\text{MgFe}_2\text{O}_4$ <sup>b</sup>	$\text{K}_2\text{CO}_3$	63	39	61

<sup>a</sup> Reaction conditions (solventless): benzyl alcohol (9.6 mmol), catalyst (4.1  $\mu\text{mol}$  of Au), base (0 or 0.33 mmol),  $100\text{ }^\circ\text{C}$ , 2 atm of  $\text{O}_2$ , 2.5 h. <sup>b</sup> The support was calcined at  $800\text{ }^\circ\text{C}$  for 4 h.

permits an instantaneous separation using a permanent magnet ( $\text{Nd}_2\text{Fe}_{14}\text{B}$ ) and immediate re-dispersion when the magnetic field is removed.

The  $\text{Au}/\text{MgFe}_2\text{O}_4$  catalyst was applied in the oxidation of benzyl alcohol in the absence and presence of an additional base co-catalyst. The results are displayed in Table 1.

According to the results obtained, the support does not exhibit any catalytic activity before or after calcination at  $800\text{ }^\circ\text{C}$  (entries 1 and 5). However, the immobilisation of PVA-stabilised Au NPs on  $\text{MgFe}_2\text{O}_4$  provided a new catalyst able to oxidise benzyl alcohol in the absence of an additional base (entries 2 and 6). In previous studies performed in our group, PVA-stabilised Au NPs supported on silica-coated magnetite reached no more than 1.7% conversion under the same conditions, in the absence of a base.<sup>25</sup> The partial substitution of  $\text{Mg}^{2+}$  by  $\text{Fe}^{2+}$  ions on the  $\text{MgFe}_2\text{O}_4$  support crystal structure revealed a catalytic performance enhancement, as the reaction conversion reached 35% and the selectivity for benzaldehyde was 59% (entry 2). It is important to notice that benzoic acid was the only by-product and benzylbenzoate was not observed in the reaction products. The immobilisation of PVA-stabilised Au NPs on the support previously calcined at  $800\text{ }^\circ\text{C}$  decreased the conversion to 24%, but enhanced the selectivity to benzaldehyde to 94%. Increasing the reaction pressure from 2 to 4 atm of  $\text{O}_2$  for a reaction similar to the one described in Table 1 entry 2 did not cause changes in the catalytic activity (conv. = 34% and sel. = 58%) and therefore all experiments were performed at lower pressure.

The influence of the presence of an additional base co-catalyst to the reaction medium was studied in an attempt to improve the catalyst activity. Two bases with different alkaline forces were tested, potassium hydroxide and potassium carbonate. We have observed that the addition of sub-stoichiometric amounts of  $\text{K}_2\text{CO}_3$  improved the catalyst activity as well as changed the selectivity to benzoic acid. In the presence of an additional base, the conversion rose to 62% and the selectivity to 64% of benzoic acid (entry 3). The addition of KOH did not show significant change in the activity or selectivity (entry 4) compared to the reaction in the absence of a base. When such a strong base was used, the catalyst deteriorated, causing metal leaching to the reaction medium.

Considering the performance of the catalyst in the presence of  $\text{K}_2\text{CO}_3$  and the changes in selectivity for benzoic acid production, kinetics experiments were performed to understand how the reaction time and conversion was affecting the product distribution. The oxidation of benzyl alcohol was repeated in several experiments, each one being ceased at a different reaction time, and the conversion and selectivity as a function of reaction time are displayed in Fig. 3. The reaction conversion reached 86% in about 10 h of reaction, and it did not change when the reaction time was prolonged to 24 h. Benzaldehyde is formed preferentially at a very low conversion, and benzoic acid is the main product after reaching 40% conversion. Interestingly, the selectivity to the acid is essentially constant after 2.5 h of reaction.

At this point, we can partially conclude that the substitution of  $\text{Fe}^{2+}$  ions in the ferrite structure of magnetite by the more

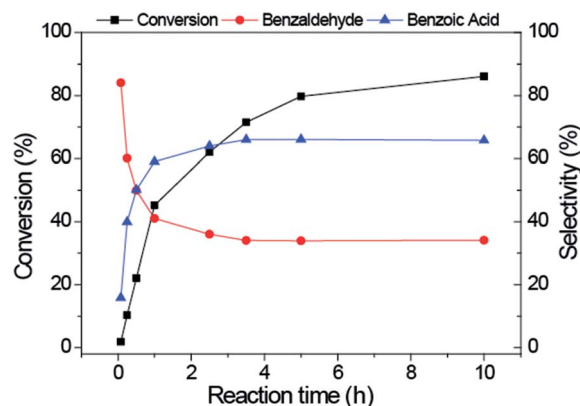


Fig. 3 Kinetic studies of  $\text{Au}/\text{MgFe}_2\text{O}_4$  catalyst in the presence of  $\text{K}_2\text{CO}_3$ .

alkaline  $\text{Mg}^{2+}$  ions caused a significant promotional effect on the oxidation of benzyl alcohol by Au NPs, most probably due to the influence of the support basicity, as expected for other basic support such as  $\text{MgO}$ , which enhances the substrate activation over the catalyst surface.<sup>15</sup> In addition, it is worth noting that the addition of sub-stoichiometric amounts of  $\text{K}_2\text{CO}_3$  further improved the catalyst activity, as already demonstrated for other oxide-supported gold nanoparticles.<sup>12</sup> Zheng *et al.*<sup>12</sup> concluded that basicity is necessary to boost the catalytic activity of Au NPs in the selective oxidation of alcohols, but the role of the small amount of carbonate promoter used in the oxidative process was not elucidated.

Searching for the improvement of the catalytic activity, we have decided to further increase the amount of  $\text{Mg}^{2+}$  ions in the support by preparing a composite material comprised of  $\text{MgFe}_2\text{O}_4$  and  $\text{MgO}$ . The previously prepared  $\text{MgFe}_2\text{O}_4$  was then used as starting material for a second process in which the  $\text{MgO}/\text{MgFe}_2\text{O}_4$  support was prepared by an impregnation method<sup>18</sup> and calcined at  $800\text{ }^\circ\text{C}$  in air. Fig. 4a shows the XRD pattern of the product obtained, which was indexed to two crystalline phases: one composed of  $\text{MgFe}_2\text{O}_4$  (JCPDS PDF #89-1935) and another corresponding to  $\text{MgO}$  (JCPDS PDF #45-946). The estimated volume fraction of the phases, inferred by the Rietveld refinement of the XRD data, was about 90.1% to cubic  $\text{MgO}$  and 9.9% to  $\text{MgFe}_2\text{O}_4$ . The  $\text{MgO}/\text{MgFe}_2\text{O}_4$  support was mixed with a PVA-stabilised Au NPs aqueous solution for the immobilisation process, which caused hydrolysis of part of the  $\text{MgO}$  into the  $\text{Mg}(\text{OH})_2$  phase (Fig. 4b). The estimated volume fraction of the phases after the Rietveld refinement was about 72.8% to cubic  $\text{MgO}$ , 17.9% to hexagonal  $\text{Mg}(\text{OH})_2$  and 9.3% to cubic  $\text{MgFe}_2\text{O}_4$ .

The low concentration and small size of the Au NPs hampered the observation of gold diffraction peaks in the XRD of the  $\text{Au}/\text{MgO}/\text{MgFe}_2\text{O}_4$  catalyst (Fig. 4b), but the transmission electron microscopy (TEM) analysis clearly shows well-dispersed Au NPs with a mean diameter of  $4.0 \pm 1.1\text{ nm}$  (Fig. 5). The UV-Vis absorption spectrum of the aqueous Au NPs colloidal solution exhibits an intense absorption at 530 nm (Fig. 6a), which is characteristic of the gold surface plasmon resonance band.<sup>26</sup> The impregnation of the Au NPs on the

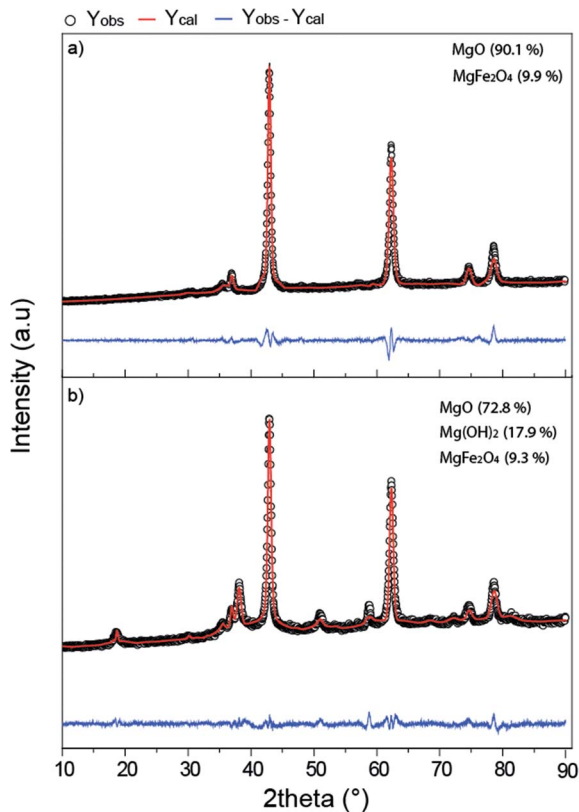


Fig. 4 X-ray diffraction patterns of MgO/MgFe<sub>2</sub>O<sub>4</sub>: (a) before and (b) after the impregnation of Au NPs.

support can be inferred by the appearance of the characteristic plasmon band of the Au NPs in the UV-Vis absorption spectrum of Au/MgO/MgFe<sub>2</sub>O<sub>4</sub> (Fig. 6b) and its absence in the corresponding spectrum of the support (Fig. 6c). The surface plasmon resonance band shifted to the red ( $\lambda_{\text{max}} = 548 \text{ nm}$ ) and broadened as compared with the band of the colloidal gold solution, which may suggest agglomeration of the Au NPs after immobilisation on the support.

The modification of the magnesium ferrite with magnesium oxide further increased the catalytic activity of the supported Au NPs for the oxidation of benzyl alcohol, as summarised in Table 2. The MgFe<sub>2</sub>O<sub>4</sub> support was inactive (Table 1, entry 1); however, the aforementioned modification with MgO caused a noticeable

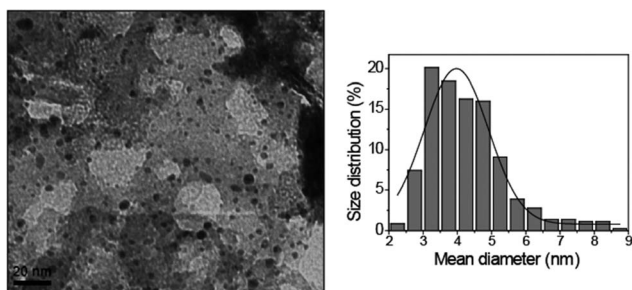


Fig. 5 TEM images of Au/MgO/MgFe<sub>2</sub>O<sub>4</sub> catalysts prepared by immobilisation of Au NPs and the corresponding size distribution histograms.

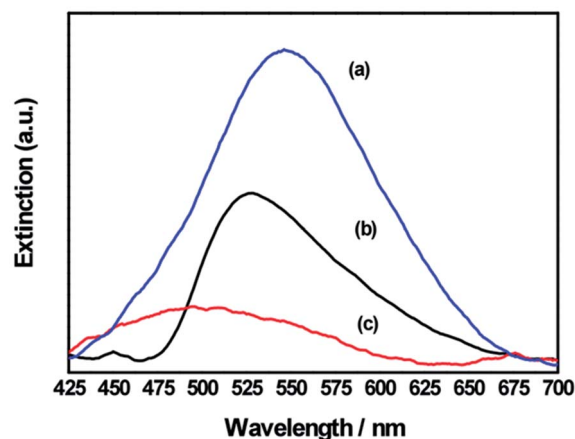


Fig. 6 UV-Vis absorption spectra of (a) Au/MgO/MgFe<sub>2</sub>O<sub>4</sub> catalyst (solid) (b) Au NPs aqueous colloidal solution, and (c) MgO/MgFe<sub>2</sub>O<sub>4</sub> support (solid).

Table 2 Oxidation reaction of benzyl alcohol using Au/MgO/MgFe<sub>2</sub>O<sub>4</sub><sup>a</sup>

Entry	Catalysts	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Benzoic acid
8	MgO/MgFe <sub>2</sub> O <sub>4</sub>	4	94	6
9	Au/MgO/MgFe <sub>2</sub> O <sub>4</sub>	51	58	42
10	Au/MgO/MgFe <sub>2</sub> O <sub>4</sub> <sup>b</sup>	86	25	75

<sup>a</sup> Reaction conditions (solventless): benzyl alcohol (9.6 mmol), catalyst (4.1  $\mu\text{mol}$  of Au), 100 °C, 2 atm of O<sub>2</sub>, 2.5 h. <sup>b</sup> K<sub>2</sub>CO<sub>3</sub> (0.33 mmol).

conversion of benzyl alcohol (4%) in benzaldehyde (Table 2, entry 8). The immobilisation of PVA-stabilised Au NPs on the MgO/MgFe<sub>2</sub>O<sub>4</sub> support caused a remarkable increase in the catalytic activity. The reaction conversion reached *ca.* 50% without additional base, and the selectivity has not changed, producing a mixture of benzaldehyde and benzoic acid (Table 2, entry 9). The Au/MgO/MgFe<sub>2</sub>O<sub>4</sub> catalyst was also tested in the presence of an additional base co-catalyst, which caused an increase of the reaction conversion to 86% (Table 2, entry 10). At this high conversion, benzoic acid was the major product obtained with 75% selectivity.

The stability of the catalyst was assessed by using the same catalyst portion in five successive reactions of oxidation of benzyl alcohol (Fig. 7). In the recycle experiments without an additional base, in each successive run, the catalyst was washed three times with acetone; however, in the experiments performed with K<sub>2</sub>CO<sub>3</sub>, the catalyst was washed with water to remove the base from the previous run, and then three times with acetone. The catalyst tested with and without the additional base co-catalyst exhibited remarkable differences. The magnesium oxide/magnesium ferrite composite (MgO/MgFe<sub>2</sub>O<sub>4</sub>) exhibited a significant promotional effect on the activity of PVA-stabilised Au NPs in the oxidation of benzyl alcohol. The catalyst exhibited a conversion higher than 50% in the first cycle even without an additional base, but there was a

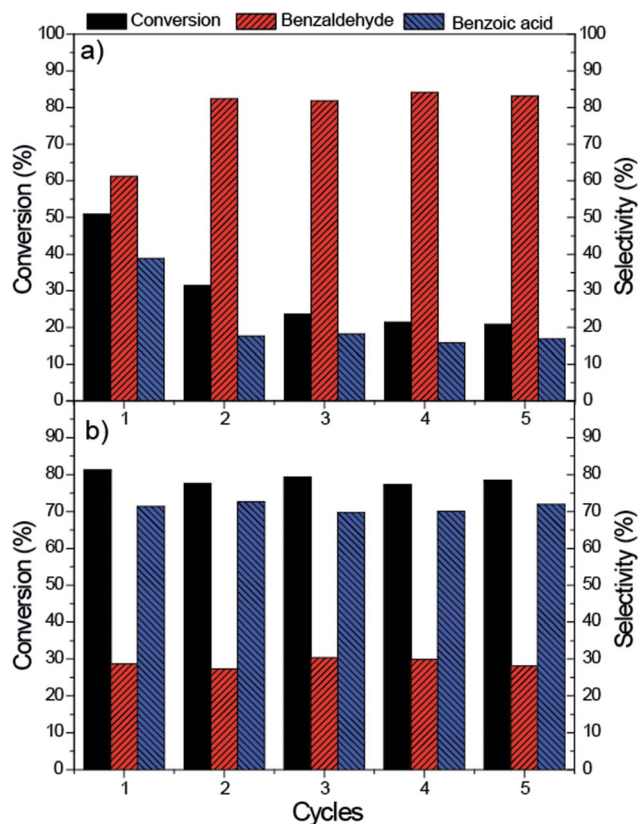


Fig. 7 Recycling of the Au/MgO/MgFe<sub>2</sub>O<sub>4</sub> catalyst in the oxidation of benzyl alcohol (a) without base and (b) in the presence of K<sub>2</sub>CO<sub>3</sub>.

considerable loss of activity in successive runs. Meanwhile, the same catalyst in the presence of K<sub>2</sub>CO<sub>3</sub> reached an 80% conversion and remained stable with similar conversion and selectivity in the five successive runs (Fig. 6b). It is important to notice that, in the presence of sub-stoichiometric amounts of K<sub>2</sub>CO<sub>3</sub>, the selectivity was changed to the preferential production of benzoic acid. FAAS analyses of the spent catalysts after the fifth run confirmed the leaching of *ca.* 50% of the Au in the recycled material used without an additional base, lending credence to the observed reduction of activity in successive runs. For the catalysts used in the presence of K<sub>2</sub>CO<sub>3</sub>, no leaching was detected, and the catalytic performance was preserved. The catalysts used in the presence of K<sub>2</sub>CO<sub>3</sub> did not show any sign of deactivation and can be, in principle, used in further reaction cycles. The amount of K<sub>2</sub>CO<sub>3</sub> added to the reaction system, responsible for the catalyst activation and for the improvement of the stability, corresponds to only 3.4 mol% with respect to the substrate. Any conclusion about the promoting effect of such a small amount of carbonate on the oxidative process would be merely speculative. However, the extra stabilization provided by the addition of K<sub>2</sub>CO<sub>3</sub> in the recycling experiments may be related to the MgO–Mg(OH)<sub>2</sub> equilibrium. MgO could be easily converted into Mg(OH)<sub>2</sub> in the presence of water released during the oxidation reaction, which would result in a poorer catalyst. Estrada *et al.*<sup>15</sup> reported that Au NPs supported on the MgO surface are *ca.* 50% more active in the oxidation of benzyl alcohol as compared to those on

Mg(OH)<sub>2</sub>, mainly due to the much higher capacity of the dehydrated MgO surface to adsorb and to activate the substrate benzyl alcohol.

## Conclusions

We have performed a systematic study on the synthesis and the catalytic activity of PVA-stabilised Au NPs supported on magnesium ferrite and magnesium oxide/magnesium ferrite composites for the oxidation of benzyl alcohol. The presence of Mg<sup>2+</sup> ions in the ferrite structure did not attribute any catalytic activity to the support only, but it was found to improve the catalytic activity of supported Au NPs to *ca.* 35% conversion in the absence of an additional base. After modifying the support with MgO, the catalytic activity of supported Au NPs was further improved to *ca.* 50% conversion, but the catalyst deactivated in successive recycling tests. The addition of a sub-stoichiometric amount of K<sub>2</sub>CO<sub>3</sub> significantly increased the catalytic activity to *ca.* 80% conversion and changed the selectivity for the acid production (>70%), enabling successive cycles with no loss of performance and without metal leaching.

## Acknowledgements

The authors acknowledge support from FAPESP and CNPq.

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