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## FULL PAPER

## Highly efficient and green oxidation of alkanes and alkylaromatics with hydrogen peroxide catalysed by silver and vanadyl on mesoporous silica-coated magnetite

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Hassan Hosseini-Monfared, Department of Chemistry, University of Zanjan, Zanjan 45195-313, Iran. Email: monfared@znu.ac.ir A heterogeneous catalyst (FeSi/Ag/VO) based on silver and vanadyl as active sites and mesoporous silica-coated nanospheres of magnetite (Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>) as support was successfully prepared by deposition of Ag nanoparticles and the covalent grafting of vanadyl(IV) acetylacetonate on Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>. The catalyst exhibited excellent activity for the oxidation of alkanes, benzene and alkylaromatics using green oxidant H<sub>2</sub>O<sub>2</sub> and oxalic acid in acetonitrile at 60 °C.

## KEYWORDS

heterogeneous catalyst, hydrogen peroxide, hydroxylation, magnetic nanocomposite, mesoporous silica, phenols, silver, vanadium oxide

## **1 | INTRODUCTION**

Oxidation reactions remain challenging in the practical preparation of both intermediates and fine chemicals. Effective molecular catalysts are available for the major reaction types such as epoxidation, alcohol oxidation or oxidation of heteroatoms, but the major drawbacks of homogeneous catalysts is the difficulty in separating the relatively expensive catalysts from the reaction mixture at the end of the process.<sup>[1]</sup> The possible contamination of catalysts in products also restricts their use in industry. Efficient anchoring of these catalysts on supports may overcome these drawbacks.<sup>[2]</sup> Immobilized molecular catalysts may also allow better control of the active site architecture and accessibility. The active sites seem most strictly defined in covalently anchored catalysts, and porous supports allow maximization of the efficiency of the catalysts by ensuring optimal accessibility.<sup>[1]</sup>

Recently, magnetic particles have been extensively employed as alternative catalyst supports, in view of their convenient catalyst recycling, high surface area resulting in high catalyst loading capacity, high dispersion and outstanding stability.<sup>[3,4]</sup> It has been reported that silica as a protecting shell can be utilized to coat  $Fe_3O_4$  particles to form a coreshell ( $Fe_3O_4@SiO_2$ ) structure.<sup>[5]</sup> Magnetite–mesoporous silica ( $Fe_3O_4@m-SiO_2$ ) nanocomposites have attracted tremendous scientific and technological interest because magnetic characteristics can be incorporated into mesoporous structures with large pore volume and high surface area.<sup>[6]</sup> Meanwhile, the silica shell can prevent the aggregation of  $Fe_3O_4$  particles and provide numerous surface Si–OH groups for further modification.<sup>[7]</sup>

As a relatively inexpensive noble metal, silver nanoparticles (Ag NPs) have been applied in a variety of catalytic reactions, such as selective butadiene epoxidation, ethanol oxidation and selective NO<sub>x</sub> reduction.<sup>[8]</sup> Hu *et al.* have developed a simple solution-phase method to synthesize Ag-coated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> composite microspheres through the Ag mirror reaction.<sup>[9]</sup> Li and co-workers have reported a facile method to generate core-shell structured Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Ag magnetic nanocomposite with the aid of polyvinylpyrrolidone as both reductant and stabilizer.<sup>[10]</sup> It has been found that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Ag nanospheres exhibit enhanced catalytic reduction efficiency for rhodamine B and eosin Y compared with pure Ag or  $Fe_3O_4$  NPs.<sup>[11]</sup> It has been proved that supported silver catalysts possess a stable activity for CO oxidation at low temperatures.<sup>[12]</sup> Our previous studies also showed that Ag NP-decorated graphene oxide catalyses aerobic oxidation of benzyl alcohol.<sup>[13]</sup> However, silver has rarely been considered as a catalyst for the selective oxidation of saturated hydrocarbons.

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Over the past decade, metal acetylacetonate complexes have emerged as versatile catalysts for a broad range of industrially and academically interesting reactions.<sup>[14]</sup> Vanadyl (IV) acetylacetonate ([VO(acac)<sub>2</sub>]) is a typical efficient catalyst extensively employed for various oxidative transformations.<sup>[15]</sup> Immobilization of [VO(acac)<sub>2</sub>] on mesoporous silicas,<sup>[15,16]</sup> amine-functionalized clay,<sup>[17,18]</sup> carbon materials<sup>[19]</sup> or mesoporous carbon nitride,<sup>[20]</sup> via reactions between the carbonyl group of the acetylacetonate ligand and the amino groups of the solid surfaces, provides an effective strategy to utilize [VO(acac)<sub>2</sub>]. Supported metal acetylacetonate complexes have been found to be more effective and selective than their homogeneous counterparts.<sup>[21]</sup>

Co-catalysts or additives which are in reality the ligands for catalysts can improve the catalyst impact. It has been reported that oxidation of cyclohexane with hydrogen peroxide and [VO(acac)<sub>2</sub>] is achieved efficiently with oxalic acid and glyoxal added as additives.<sup>[22]</sup> Carboxylic acid takes an active role in the oxidation of polypropylene.<sup>[23]</sup> White and co-workers<sup>[24]</sup> demonstrated that by acting as ligands for the metal, carboxylic acids overcome a range of substrate biases (electronic, steric and stereoelectronic) in C—H hydroxylation reactions which are catalysed by a non-heme iron complex. The partial oxidation of toluene by hydrogen peroxide was also achieved with catalytic amounts of [VO(acac)<sub>2</sub>] in acetic acid.<sup>[25]</sup>

Although there have been substantial advances in the oxidation of hydrocarbons, the development of effective and selective methods for the catalytic functionalization of inactive carbon–hydrogen bonds in saturated hydrocarbons still remains a major challenge in oxidation chemistry.<sup>[26]</sup> In the study reported here, we used the synergic effect of Ag NPs and [VO(acac)<sub>2</sub>] supported on mesoporous silica-coated Fe<sub>3</sub>O<sub>4</sub> NPs for the oxidation of various hydrocarbons including alkanes, benzene and alkylaromatics with hydrogen peroxide. Hydrogen peroxide is probably the best terminal oxidant after dioxygen with respect to environmental and economic considerations.<sup>[27]</sup>

## 2 | EXPERIMENTAL

## 2.1 | Materials and instrumentation

Iron (III) chloride hexahydrate (VMR, >99%), iron (II) chloride tetrahydrate (Merck, >99%), oleic acid (VMR, 96%), tetraethoxysilane (TEOS; Merck, 99%), cetyltrimethylammonium bromide (CTAB; Merck, 97%), (3-aminopropyl) triethoxysilane (Fluka, 98%), cyclohexane, [VO(acac)<sub>2</sub>] (Merck, 98%) and all other chemicals were obtained commercially from Merck or Fluka and used without further purification. Deionized water was used for all experiments.

The reaction products of the oxidation were determined and analysed using an HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenylmethylsiloxane, 30 m  $\times$  320 µm  $\times$  0.25 µm) with a flame-ionization detector. GC–MS analysis of the oxidation products was conducted with a PerkinElmer Clarus SQ8S apparatus.

<sup>1</sup>H NMR spectra of reaction mixtures (without purification) were recorded with a Bruker 250 MHz spectrometer. Fourier transform infrared (FT-IR) spectra were obtained using a PerkinElmer 597 spectrophotometer after making pellets with KBr powder. Powder X-ray diffraction (XRD) patterns were collected using a D8ADVANCE instrument (Bruker, Germany), with a wavelength of 1.5406 Å (Cu K $\alpha$ ), voltage of 40 kV and current of 40 mA. The size and morphology of solid compounds were recorded using a Hitachi F4160 scanning electron microscopy (SEM) instrument operated at an accelerating voltage of 10 kV. Magnetization measurements were performed at room temperature using a vibrating sample magnetometer, in the Development Center of the University of Kashan (Iran).

# 2.2 | Preparation of hydrophobic magnetite (Fe $_3O_4$ ) NPs

Hydrophobic magnetite NPs were synthesized based on a modification of a published one-pot chemical co-precipitation method.<sup>[28]</sup> First, deionized water was purged with nitrogen gas for 10 min. Then, 4.80 g of FeCl<sub>3</sub>·6H<sub>2</sub>O, 2.00 g of FeCl<sub>2</sub>·4H<sub>2</sub>O and 0.85 ml of oleic acid were added to 30 ml of deionized water under nitrogen atmosphere with vigorous stirring. The mixture solution was heated to 90 °C. Then, 20 ml of ammonium hydroxide (14 wt%) was added rapidly to the solution, and it immediately turned black. The reaction was kept at 90 °C for 2.5 h and then allowed to cool to room temperature. The black precipitate was collected using an external magnet.

## 2.3 | Mesoporous silica-coated magnetite NPs (Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>)

As-synthesized Fe<sub>3</sub>O<sub>4</sub> NPs were coated with mesoporous silica by employing the modified Stöber method and using CTAB as a template.<sup>[29]</sup> CTAB also serves as a stabilizing surfactant for the transfer of hydrophobic Fe<sub>3</sub>O<sub>4</sub> nanocrystals to the aqueous phase. In a typical procedure, 0.350 g of oleic acid-stabilized magnetite NPs dispersed in 30 ml of chloroform was added to 100 ml of an aqueous CTAB (2.0 g) solution and the resulting solution stirred vigorously for 30 min. The formation of an oil-in-water microemulsion resulted in a turbid brown solution. Heating the brown solution at 60 °C for 20 min induced evaporation of the chloroform, and generating an aqueous dispersion of NPs. The resulting mixture solution was added to a mixture of 200 ml of water and 5 ml of 2 M NaOH solution, and the mixture was heated to 70 °C. Then ethyl acetate (10 ml) was successively added to the diluted aqueous solution containing the magnetite NPs, and, after 10 min, TEOS

(3 ml) was added dropwise. The resulting mixture was stirred for 3 h and the precipitate magnetically separated and thoroughly washed with ethanol to remove unreacted species and surfactant, then oven-dried in air at 60 °C for 24 h.

## 2.4 | Synthesis of Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag

A simple electroless plating process was carried out to deposit Ag NPs on the surface of  $Fe_3O_4@m-SiO_2$ .<sup>[11]</sup> AgNO<sub>3</sub> (0.034 g) was dissolved in ethanol (150 ml) by ultrasonication in a polypropylene flask and then a solution of  $Fe_3O_4@m-SiO_2$  NPs (0.12 g) in ethanol (50 ml) was added. The mixture was stirred for 50 min at 50 °C with a magnetic stirrer and then a solution of dibutylamine (0.015 g ml<sup>-1</sup>, 1.0 ml) in ethanol was added to reduce Ag<sup>+</sup> to Ag NPs on the surface of  $Fe_3O_4@m-SiO_2$  NPs. The ratio of dibutylamine to AgNO<sub>3</sub> was maintained at 1:1. The mixture was stirred for 3 h at 50 °C. Finally, the products were magnetically separated, washed several times with ethanol and dried at 60 °C under vacuum.  $Fe_3O_4@m-SiO_2/Ag$  was obtained by calcination at 550 °C for 6 h to remove the organic materials.

## 2.5 | Synthesis of [VO(acac)<sub>2</sub>] covalently anchored onto amine-functionalized Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag

Following a reported procedure,<sup>[30]</sup> as-synthesized  $Fe_3O_4@m-SiO_2/Ag$  (0.6 g) was added to a solution of (3-aminopropyl)triethoxysilane (0.6 ml, 5 mmol) in dry toluene (100 ml) and refluxed for 20 h. Then [VO(acac)\_2] (0.099 g, 0.375 mmol) was added into the solution, which was refluxed for another 20 h. The catalyst was filtered off and washed successively with water, ethanol and acetone until the washings were colourless, and dried in an oven at 110 °C for 24 h. The prepared  $Fe_3O_4@m-SiO_2/Ag/VO$  (acac)<sub>2</sub> composite is denoted as FeSi/Ag/VO.

#### 2.6 | Catalytic oxidation of cyclohexane with $H_2O_2$

The catalytic experiments were carried out at 60 °C in a round-bottom 25 ml glass flask reactor equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, the flask was charged with a suspension of substrate (2 mmol), catalyst (10.0 mg) and oxalic acid (0.10 mmol) as co-catalyst in 5 ml of acetonitrile. After heating for 5 min under stirring, the oxidation reaction was started with the addition of 4.5 mmol aqueous hydrogen peroxide (12.5 mol  $1^{-1}$ ). Usually, the reaction was carried out for 8 h under atmospheric pressure. Aliquots of the reaction mixture (0.2 ml) were withdrawn periodically during the course of the reaction using a syringe. Each aliquot was analysed by GC after addition of toluene as internal standard. The identification of the oxidation products was performed by comparison with the retention times of commercial cyclohexanol and cyclohexanone, <sup>1</sup>H NMR spectroscopy or GC-MS.

In order to determine the content of cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide, each sample was analysed by GC twice, before and after addition of PPh<sub>3</sub> (in the presence of PPh<sub>3</sub>, cyclohexyl hydroperoxide is quantitatively transformed into cyclohexanol; then, its true content can be calculated as the difference between the cyclohexanol concentration before and after PPh<sub>3</sub> addition).<sup>[31]</sup> It was revealed that the yield of peroxide was negligible.

For recycling experiments, after completion of the reaction, the nanocatalyst was recovered using a magnet, washed with acetonitrile, dried and reused without further purification.

#### **3** | **RESULTS AND DISCUSSION**

#### 3.1 | Synthesis and characterization

Synthesis of the nanocomposite was performed as shown in Scheme 1. The magnetite NPs were synthesized and stabilized with oleic acid using a co-precipitation method.<sup>[28]</sup> Then, mesoporous silica was used to coat the synthesized  $Fe_3O_4$  NPs by employing the modified Stöber method with CTAB used as a template.<sup>[29]</sup> Ag NPs were deposited on  $Fe_3O_4$ @m-SiO<sub>2</sub> by a simple electroless plating process.<sup>[11]</sup> Finally, [VO(acac)<sub>2</sub>] was covalently anchored onto aminefunctionalized Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag to afford FeSi/Ag/VO.<sup>[30]</sup>

Figure 1 shows FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/ Ag and FeSi/Ag/VO. A strong absorption band at 595  $cm^{-1}$ is related to the vibrations of the Fe-O functional group, which shows that the phase of as-prepared  $Fe_3O_4$  particles is mainly magnetite.<sup>[32]</sup> For Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag and FeSi/ Ag/VO, the shoulder at  $638 \text{ cm}^{-1}$  might be assigned to the formation of some amount of oxidized maghemite on the magnetite surface after calcination at 550 °C for 6 h. In the Fe-O range, maghemite shows broad FT-IR bands at 668, 630 and 442 cm<sup>-1.[33,34]</sup> The broad characteristic band at  $3424 \text{ cm}^{-1}$  (not shown) could be assigned to O–H stretching vibration arising from the Fe-OH groups on Fe<sub>3</sub>O<sub>4</sub> NPs and coating oleic acid and adsorbed water.[35] The peaks around 2927 and 2852 cm<sup>-1</sup> are assignable to asymmetric/symmetric vibrations of C-H in -CH2- of oleic acid[36] and intramolecular hydrogen bond derived from OH.<sup>[37,38]</sup> The bands at 1623 and 1441  $\text{cm}^{-1}$  can be ascribed to the asymmetric and symmetric stretching vibrations of CO<sub>2</sub><sup>-</sup>, respectively. Based on the FT-IR spectra, it is concluded that oleic acid is coating



SCHEME 1 Synthesis of FeSi/Ag/VO nanocomposite



FIGURE 1  $\,$  FT-IR spectra of (a) Fe\_3O\_4, (b) Fe\_3O\_4@m-SiO\_2/Ag and (c) FeSi/Ag/VO

the surface of the magnetite NPs.<sup>[39]</sup> The spectrum of Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag shows broad characteristic antisymmetric ( $\nu_{as}$ ) Si–O–Si vibration bands<sup>[40]</sup> of the [SiO<sub>4</sub>] unit observed around 1038–1097 cm<sup>-1</sup>, suggesting the successful coating of silica layer on the Fe<sub>3</sub>O<sub>4</sub> surface. The V=O stretching band of FeSi/Ag/VO at about 1000 cm<sup>-1</sup> is not seen due to the overlap by the very strong and broad band of silica. In addition to the CH and CH<sub>3</sub> stretching bands around 3000 cm<sup>-1</sup>, the bands appearing in the range 1554–1587 cm<sup>-1</sup> are assigned to  $\nu$ (C=O) of the supported [VO(acac)<sub>2</sub>] in FeSi/Ag/VO.<sup>[41]</sup>

The field-emission SEM images of  $Fe_3O_4$ @SiO<sub>2</sub> and FeSi/Ag/VO nanocomposites show that the particles are non-aggregated and almost monodispersed spheres with a smooth surface (Figure 2a–d). The morphological features such as the spherical shape and non-aggregation are found to be retained in the case of FeSi/Ag/VO, similar to Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. After applying FeSi/Ag/VO five times in the catalytic oxidation of cyclohexane (Section 3.2), its size and morphology remain intact, which shows its stability in the oxidation medium (Figure 2e and f). However, the surfaces of the particles are not perfectly smooth after five recycles.

The Fe<sub>3</sub>O<sub>4</sub> NPs and FeSi/Ag/VO show no hysteresis curves at room temperature (Figure 3), confirming their paramagnetic nature. The magnetic saturation values of Fe<sub>3</sub>O<sub>4</sub> and FeSi/Ag/VO are 49.2 and 34.6 emu g<sup>-1</sup>, respectively. After surface modification of magnetite there is some decrease in the saturation magnetization, which is attributed to the presence of the non-magnetic materials. Nevertheless, the nanocomposite can be enriched in 30 s upon the application of an external magnetic force (Figure 3, inset).

The crystal structures and the phase purity of Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag and FeSi/Ag/VO were determined using XRD. Figure 4(a) shows the wide-angle XRD pattern of Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub> NPs. A broad reflection at  $2\theta = 20-25^{\circ}$  suggests an amorphous structure of the mesoporous silica matrix in Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>, and all the reflection peaks of the product can be easily indexed to a crystalline cubic spinel



 $\label{eq:FIGURE 2} Field-emission SEM images of (a, b) Fe_3O_4@SiO_2, (c, d) FeSi/Ag/VO and (e and f) FeSi/Ag/VO after five recycles$ 



**FIGURE 3** Magnetization curves of (a) Fe<sub>3</sub>O<sub>4</sub> and (b) FeSi/Ag/VO. Inset: (a) dispersion of FeSi/Ag/VO NP in the reaction solution and (b) FeSi/Ag/ VO NPs adsorbed on the wall of sample tube using an external magnet

structure of Fe<sub>3</sub>O<sub>4</sub>. In the case of Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag, besides the characteristic diffraction of Fe<sub>3</sub>O<sub>4</sub> microspheres, the obvious diffraction peaks at  $2\theta = 37.9^{\circ}$ , 44.1°, 64.3° and 77.2° can be readily indexed to face-centred cubic structure of Ag (Figure 4b).<sup>[11]</sup> The XRD patterns of Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag and FeSi/Ag/VO (Figure 4c) are very similar.

The isotherms of FeSi/Ag/VO are type IV BET isotherms with a hysteresis loop (Figure S1 in the supporting information), demonstrating the mesoporous characteristics of FeSi/Ag/VO. The specific areas and pore sizes were calculated using the BJH method. As a result, for FeSi/Ag/VO, the average pore size and BET surface area are 6.87 nm and  $63 \text{ m}^2 \text{ g}^{-1}$ , respectively.

## 3.2 | Catalytic studies

Oxidation of cyclohexane with  $H_2O_2$  was chosen as a representative reaction and the effect of catalyst, oxidant,



FIGURE 4 XRD patterns of (a)  $Fe_3O_4@m-SiO_2$ , (b)  $Fe_3O_4@m-SiO_2/Ag$  and (c) FeSi/Ag/VO



additive and support was examined (Table 1). It is found that the presence of oxidant, catalyst and oxalic acid (as additive) is essential for the oxidation (Table1, entries 1-3). Oxalic acid is a kind of weak acid, and, in this catalytic system, it may provide protons to active species. To check this proposal, we studied the oxidation of cyclohexane by H<sub>2</sub>O<sub>2</sub> in a CH<sub>3</sub>CN-oxalic acid mixture with varying amounts of oxalic acid ranging from 0.10 to 1.0 mmol. From Table 1, we observe that there is a maximum conversion as a function of amount of oxalic acid (entries 4-6), as is the case for the yields of cyclohexanol and cyclohexanone. The presence of protons has accelerated the oxidation, but there is no substantial increase of activity with further increase of oxalic acid concentration. It has been reported that carboxylic acid (stearic acid) takes an active role in oxidation of polypropylene<sup>[23]</sup> with the possibility of involvement in an increase of the initiation rate by enhancement of bimolecular decomposition of hydroperoxides due to changing of the polarity of the reaction environment or increasing the initiation rate by direct catalysis of hydroperoxide decomposition. Alternatively, it is reasonable to propose that acetic acid may take part in cyclohexane oxidation in other ways, such as complexing with the vanadium catalytic active centre at high acetic acid concentration or forming peroxyacetic acid.[25]

The reaction temperature changes markedly the catalyst activity in the oxidation of cyclohexane. The catalyst shows activity at temperatures higher than 45 °C and the conversion increases on increasing the temperature (entries 6 and 7). The lowest temperature of 60 °C was selected in order to manage the H<sub>2</sub>O<sub>2</sub> decomposition. While FeSi/Ag/VO could catalyse the oxidation of cyclohexane up to 99% conversion, the support Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@m-SiO<sub>2</sub>/Ag could catalyse it up to 35 and 50%, respectively, for the same conditions (entries 6, 8 and 9).

TABLE 1	Catalytic	oxidation	of c	yclohexane	with	$H_2O_2^a$
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Entry	Catalyst	Oxidant/additive	Conversion (%)
1	None	$H_2O_2/H_2C_2O_4$	0
2	FeSi/Ag/VO	None/H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0
3	FeSi/Ag/VO	H <sub>2</sub> O <sub>2</sub> /none	0
4	FeSi/Ag/VO	$H_2O_2/H_2C_2O_4^{\ b}$	77
5	FeSi/Ag/VO	$H_2O_2/H_2C_2O_4^{\ c}$	92
6	FeSi/Ag/VO	$H_2O_2/H_2C_2O_4$	99
7	FeSi/Ag/VO	$H_2O_2/H_2C_2O_4{}^d$	0
8	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	$H_2O_2/H_2C_2O_4$	35
9	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /Ag	$H_2O_2/H_2C_2O_4$	50

<sup>a</sup>Reaction conditions: catalyst, 0.010 g; co-catalyst (oxalic acid,  $H_2C_2O_4$ ), 1.0 mmol; cyclohexane, 2.0 mmol; CH<sub>3</sub>CN, 5 ml; aqueous 30%  $H_2O_2$ , 4.5 mmol; temperature, 60 °C; reaction time, 8 h.

<sup>b</sup>0.1 mmol oxalic acid. <sup>c</sup>0.26 mmol oxalic acid. <sup>d</sup>20°C.

FABLE 2	Oxidation of various hydrocarbons with H <sub>2</sub> O <sub>2</sub>	<sub>2</sub> catalysed by FeSi/Ag/VO <sup>a</sup>	
Entry	Substrate	Conversion (%)	Products (yield, %)
1	<i>n</i> -Hexane	100	CHO (47) (28) (12) (12) (9) (9)
			CO <sub>2</sub> H (4)
2 <sup>b</sup>		99	O OH others (47) (45) (7)
3 <sup>b</sup>		87	(53) (23) (11)
4		66	OH (66)
5		61	(41) (20) CHO
6 <sup>c</sup>		46	(33) OH (13)
7		31	CHO (31)
8	OH	14	OH CHO (14)
9		45	OH (45)
10		23	OH (23)
11	СНО	72	CO <sub>2</sub> H (72)

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<sup>a</sup>Reaction conditions: FeSi/Ag/VO, 0.010 g; oxalic acid, 1 mmol; CH<sub>3</sub>CN, 5 ml; aqueous 30% H<sub>2</sub>O<sub>2</sub>, 4.5 mmol; temperature, 60 °C; reaction time, 8 h. Naphthalene, 1 mmol; others, 2 mmol.

<sup>b</sup>Other products were the corresponding -diol, -dione and (-ol and -one) isomers.

<sup>c</sup>After 6 h.



FIGURE 5 Recycling of FeSi/Ag/VO catalyst for the oxidation of cyclohexane. For reaction conditions, see the footnote to Table 2. Averages of duplicate experiments and error bars represent the standard deviations

In order to expand the hydrocarbon scope, a linear alkane, benzene and alkylaromatics were also tested and the results are presented in Table 2. We find that *n*-hexane is oxidized at a relatively low temperature (60 °C) in the presence of oxalic acid to give a mixture of isomeric ketones and acids with an unusual distribution of regioisomers. The oxidation of *n*-hexane gives mainly 1-hexanal (47%), 3-hexanone (28%) and 2-hexanone (12%) with minor products including hexanoic acid (5%) and 2,5hexandione (9%) (Table 2, entry 1). The interesting feature of the reaction is that oxidation of both methyl and methylene groups is observed, whereas the reactivity of the more inert methyl groups is higher (the CH<sub>2</sub> groups are 80-100 times more reactive than the CH<sub>3</sub> groups). This observation, which is not in accordance with other findings,<sup>[42]</sup> clearly testifies that the alkane oxidation involves free hydroxyl radicals or, possibly, metal-oxo species. For the reaction of n-heptane with hydroxyl radical generators (the 'vanadate ion-pyrazine-2-carboxylic acid-H<sub>2</sub>O<sub>2</sub>' reagent,  $h\nu$ -H<sub>2</sub>O<sub>2</sub>, FeSO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>), the normalized selectivity parameter  $C_1:C_2:C_3:C_4$ for the relative reactivities of the hydrogen atoms in positions 1, 2, 3 and 4 of the hydrocarbon chain was found to be  $6.7:60:47:47.^{[43,44]}$  For oxidation with the H<sub>2</sub>O<sub>2</sub>- $[(LMe_3)_2Mn_2(O)_3]^{2+}$ -CH<sub>3</sub>COOH system (LMe<sub>3</sub> = 1,4,7trimethyl-1,4,7-triazacyclononane), believed to proceed via abstraction of hydrogen atoms from the alkane by the Mn=O fragment, this parameter was found to be 1.3:60:46:46.<sup>[45,46]</sup> Thus, it is reasonable to assume that alkane oxygenation with the H2O2-FeSi/Ag/VO system occurs with participation of certain hydroxyl radical species.<sup>[22,47]</sup>

Cyclohexane and cyclooctane are oxidized by  $H_2O_2$  and FeSi/Ag/VO mainly to the corresponding cyclic alcohol and ketone (Figure S2; Table 2, entries 2 and 3). We analysed the reaction solutions both before and after addition of PPh<sub>3</sub> and demonstrated that only small amounts of the

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corresponding alkyl hydroperoxides are formed.<sup>[31]</sup> A similar result (no cyclohexyl hydroperoxide after 12 h reaction time) was reported for the oxidation of cyclohexane by  $H_2O_2$  over Co-substituted heteropolytungstate catalysts.<sup>[48]</sup> Our result illustrates that selectivity and/or activity of FeSi/Ag/VO is higher than that of Cr-MCM-41,<sup>[49]</sup> [Mn(salophen)]-NaY<sup>[50]</sup> and V-MCM-41/acetic acid<sup>[51]</sup> catalysts in the oxidation of cyclohexane using hydrogen peroxide as oxidant.

To our delight, benzene is oxidized successfully to phenol in 66% yield (entry 4). One-step synthesis of benzene oxygenates with  $H_2O_2$  as green oxidant is a great challenge in modern synthetic chemistry.<sup>[52]</sup> Phenol is one of the most important intermediates of the chemical industry with a global production estimated at around 8 Mt per year, almost completely based upon the cumene process which also coproduces acetone.<sup>[53]</sup>

In the oxidation of alkylaromatic substrates, the catalytic reactions involve side-chain oxidation (entries 5-9) and the hydroxylation of the aromatic ring does not occur. No overoxidation of products is observed. Weakly electron-donating -CH<sub>3</sub> and -CH<sub>2</sub>CH<sub>3</sub> substituents slightly decrease the aromatic ring oxidation rate (entries 5-7). Strong electrondonating substituents (like -OH, entry 8) or electron-withdrawing substituents (like -NO2, not shown in Table 2) make the aromatic ring unsusceptible to oxidation by the H<sub>2</sub>O<sub>2</sub>-FeSi/Ag/VO system. Oxidation of nitrobenzene by this system was not successful. An electron-withdrawing aryl substituent<sup>[54]</sup> slightly decreases the conversion of naphthalene (23% conversion; entry 10). Benzaldehyde has the highest conversion, 72%. The high conversion of benzaldehyde is probably due to the coordination of benzaldehyde through oxygen to supported vanadyl to accelerate the oxidation.

The oxidation of aromatic C–H bonds via hydrogen atom abstraction by the active oxidizing intermediate is not possible because aromatic C–H bonds are stronger than aliphatic C–H bonds.<sup>[55]</sup> In oxidation reactions, the cleavage of the oxygen–oxygen bond in peroxides takes either of two distinct pathways, heterolytic<sup>[56]</sup> or homolytic.<sup>[57]</sup> It seems that the hydroxylation of the aromatic ring occurs via the heterolytic mechanism, involving the formation of a metalloperoxide species.

## 3.3 | Catalyst reuse

The FeSi/Ag/VO nanocomposite could be recycled at least five times without loss of catalytic properties (Figure 5). Importantly, no catalyst regeneration/reactivation is needed before reuse. The retention of the FeSi/Ag/VO structure was confirmed by FT-IR (Figures S3–S5) and SEM (Figure 2c and d) techniques. At the end of the reaction, the catalyst was separated by magnetic filtration, washed by adding acetonitrile and ultrasound for 1 min, then died and used in a fresh oxidation for five successive runs. The FeSi/Ag/VO

catalyst is truly heterogeneous and only a trace amount of vanadium (0.03%) was determined in the filtrate using inductively coupled plasma analysis.

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## 4 | CONCLUSIONS

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To summarize, the heterogeneous catalyst FeSi/Ag/VO based on silver and [VO(acac)<sub>2</sub>] immobilized on mesoporous silica-coated magnetite nanospheres demonstrates superior catalytic activity and regioselectivity in the oxidation of cycloalkanes and alkylaromatics with H<sub>2</sub>O<sub>2</sub> under mild conditions. The FeSi/Ag/VO-H<sub>2</sub>O<sub>2</sub> system produces cyclohexanone/cyclohexanol with 93% selectivity at 99% cyclohexane conversion and oxidizes benzene to phenol with 66% conversion. The FeSi/Ag/VO material behaves as a true heterogeneous catalyst and can be recycled and reused without suffering a loss of catalytic properties. The FeSi/Ag/VO-H<sub>2</sub>O<sub>2</sub>-oxalic acid-CH<sub>3</sub>CN system is a cheap and environmentally friendly oxidizing system that has potential for use in the preparation of fine chemicals and removal of hazardous aromatic compounds from industrial sewage.

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