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# Characterization and catalytic activity of a novel Fe nano-catalyst as efficient heterogeneous catalyst for selective oxidation of ethylbenzene, cyclohexene, and benzylalcohol

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1. Introduction

# ABSTRACT

In the present study, heterogeneous Fe-nano-catalyst has been covalently anchored on a modified nanoscale SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The synthesized materials were characterized by FT-IR spectroscopy, DS UV-vis, CHN elemental analysis, BET, EDS, SEM, TEM, TGA and XPS. The catalytic activity of the Fe nano-catalyst (FNC) in the oxidation of ethylbenzene, cyclohexene, and benzylalcohol was studied using *tert*-butyl hydroperoxide as oxygen source, without the need of any solvent. Oxidation of ethylbenzene, cyclohex-ene, and benzylalcohol catalyzed by (FNC) gave acetophenone, 2-cyclohexene-1-one and benzaldehyde, respectively, as major products. A suitable reaction condition has been optimized for Fe-nano-catalyst by considering the effect of various parameters such as reaction time and the amount of oxidant, different solvents, concentration of substrate for the maximum conversion of substrates and high selectivity. This catalyst can be easily prepared from inexpensive, commercially available reagent and is stable and reusable for oxidation of ethylbenzene, cyclohexene, and benzylalcohol.

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# Catalytic technologies are of utmost importance for transformation crude and cheap raw material into products with high economic value. Homogenous catalysts have many advantages such as high reactivity and selectivity, because in homogenous catalysts every single catalytic entity can act as a single active site. Despite their advantages, some of homogenous catalytic processes have not been commercialized because of difficulty encountered when attempting to separate and recovery the catalyst from the reaction mixture. Furthermore, some industrial problems such as corrosion and deposition on reactor wall are associated with these homogeneous catalysts. These disadvantages were minimized if homogeneous complexes were immobilized onto the insoluble solid supports. The majority of the heterogenized catalysts design based on anchoring transition metal on inorganic compound with

excellent chemical and thermal stability and easily accessibil-

ity. Anchoring is robust enough to endure the harsh reaction

conditions and the catalyst can be used for many times. In past decade, nanostructure has been developed that is claimed to allow greater selectivity and control in heterogeneous catalysis. Needless to say, transformation of organic compound to oxygenic compound is one of the most important reactions in the chemistry with fundamental research, general synthesis and industrial manufacturing. However, this transformation regularly leads to production of a large amount of toxic material and hence environmental pollution. Promote in the progression of new oxidation catalysts, involving transition metal complexes with Schiff base ligand [1–6], methodologies, synthesis and their applications could be one of the considerable interest of current organometallic research [7,8]. Inorganic compounds such as silica gel, clay, zeolite and mesoporous material that have been used as the support for the heterogenization of transition metal complexes with Schiff base ligands have been widely applied in selective oxidation of alcohols, alkenes and alkyl aromatics [9-13]. The development of new iron catalysts as the commercial catalyst for oxidation of hydrocarbon is attracting chemists intending to investigate new industrial access [14,15]. In the past, many chemists have paid much attention to produce benzilic and allylic ketones by oxidizing agent, such as the oxidation of ethylbenzene (EB) to acetophenon (AP) by KMnO<sub>4</sub> [16], H<sub>2</sub>O<sub>2</sub> [17–25], TBHP [17,26–31], CrO<sub>3</sub>–SiO<sub>2</sub> [32], SeO<sub>2</sub> [33]

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and  $O_2$  [34–39]. Furthermore, the use of heterogynous catalyst has afforded good to excellent conversion with good selective to 2-cyclohexene-1-one [40–48].

In order to gain an insight into the catalytic activity of a simple heterogeneous nano catalyst for the inert hydrocarbon bond oxidation with *tert*-butyl hydroperoxide (TBHP) as the oxygen donor under mild conditions and in absence of any additive, for the first time a systematic and stepwise synthesis of a heterogeneous environmental-friendly catalyst based on ferrocenecarboxaldehyde (FCA), as a commercially available molecule is reported. Here, we have demonstrated the application of a stable covalently immobilized ferrocene derivative on the surface of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed-oxide host by a linker approach and described the catalytic activity of the heterogenized ferrocene group. The synthesized materials were characterized by FT-IR spectroscopy, DS UV-vis, CHN elemental analysis, BET, EDS, SEM, TEM, TGA and XPS. The grafted complex (FCA) was employed in the oxidation of various substrates (ethylbenzene, cyclohexene and benzyl alcohol) with TBHP without additives under mild conditions. The results indicate that Fe-nano-catalyst could activate TBHP to oxidize ethylbenzene to acetophenone, cyclohexene to cyclohexene-1-one and benzyl alcohol to benzaldehyde with high conversion and selectivity under mild conditions.

# 2. Experimental

#### 2.1. Materials and instruments

All reagents were purchased from the Merck and Fluka chemical companies. Reagents were used without extra purification, but solvents were purified with standard methods. Inductively coupled plasma (ICP) measurement for Fe content evaluation was performed using a Perkin-Elmer ICP/6500. Fourier transform infrared was collected on KBr pellets using a JASCO FT/IR (680 plus) spectrometer and the position of an infrared band is given in reciprocal centimeters (cm<sup>-1</sup>). Diffuse reflectance spectra were registered on a JASCO-550 UV-vis spectrophotometer that was equipped with a diffuse reflectance attachment in which BaSO<sub>4</sub> was used as the reference. Type and quantity of the resulting products from oxidation were determined by a HP 6890/5973 GC/MS instrument and analyzed by a Shimadzu GC-16A gas chromatograph (GL-16A gas chromatograph with a  $5 \text{ m} \times 3 \text{ mm}$  OV-17 column. 60-220 °C (10 °C/min), Ini, 230 °C, Det, 240 °C). For elemental analysis a CHN-Rapid Heraeus elemental analyzer (Wellesley MA) was used. Before carrying out the nitrogen (99.999%) adsorption experiments, the sample was outgassed at 393 K for 14 h, then the experiment have been carried out at 76 K using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). The specific surface areas were calculated, using the BET (Stephen

Brunauer, Paul Hugh Emmett, and Edward Teller) method. The images of scanning electron micrograph (SEM) and transmission electron microscopy (TEM) were taken using a Philips 501 microscope and a Tecnai F30TEM operating at 300 kV, respectively. In addition, energy dispersive X-ray analysis was conducted on each sample. Size distribution in order to count nanoparticles in reverse microemulsion was measured by Zetasizer Nano-ZS-90 (ZEN 3600, MALVERN instruments).

#### 2.2. Preparation of organometallic-SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nanosized

 $SiO_2/Al_2O_3$  nanosized was used as the support prepared by the sol-gel method [45]. At first, 3.5 g of nanosized  $SiO_2/Al_2O_3$  was activated at 500 °C for 5 h under air and then refluxed with 4.3 mL of trimethoxysilylpropylamine (3-APTMS) in dry toluene (50 mL) for 24 h. The solid achieved during this process was filtered and washed off with dry methanol at 100 °C under vacuum for 5 h. Then ferrocenecarboxaldehyde (FCA) was added to a suspended solution of SiO\_2/Al\_2O\_3 supported aminopropyl (SiO\_2/Al\_2O\_3-APTMS) in dry methanol. The mixture was refluxed for 24 h to make a Fe nanocatalyst on the surface of nanoscale SiO\_2/Al\_2O\_3 (Scheme 1).

# 2.3. General procedure for oxidation ethylbenzene, cyclohexene and benzyl alcohol

In this procedure the heterogeneous catalyst (5.0 mg), the substrate (9.0 mmol) and an oxidant (9.0 mmol, 80% aqueous solution TBHP) were added in three necked round bottom flask equipped with a refluxed condenser. The mixture was stirred at desired temperature. After filtering and washing the used catalyst with solvent, the filtrate was monitored by GC analysis. The products were identified by GC–MS techniques. The conversion and selectivity were calculated with GC area normalization. Finally, comparative experiments were performed under different conditions.

# 3. Results and discussion

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# 3.1. Characterization

The heterogeneous Fe catalyst was synthesized on the nanoscale  $SiO_2/Al_2O_3$  using ferrocenecarboxaldehyde through the covalently immobilization, as illustrated in Scheme 1. The formation of Fenano-catalyst onto the  $SiO_2/Al_2O_3$  mixed oxides was verified using BET, CHN, FT-IR, UV–vis, BET, ICP, SEM, EDS, XPS, TGA and TEM. The surface area, pore size and volume of the modified support were significantly reduced compared to the parent  $SiO_2/Al_2O_3$  (this decrease indicates the decrease in interaction between adsorbate,  $N_2$  molecules, and the nano-sized  $SiO_2/Al_2O_3$  surface after modification with organic chains). The elemental analysis indicated



Scheme 1. Immobilization procedure of the immobilized Fe catalyst on the functionalized SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxide.

Ch	emical	com	position	and 1	٥hv	/sicochemica	l pro	perties	of th	ıe	immo	bilize	d f	ferrocene	grou	DS O	n the	nanos	scale	SiO	Al	03	mixed o	xides.

	-	-	-							
Catalyst	Elemental analyses (wt%) <sup>b</sup>			Organic functional	Immobilized the ferrocenec	% coordinated aliphatic	Structural parameters <sup>e</sup>			
	С	N	Fe	group (mmol/g mixed oxide) <sup>c</sup>	groups (mmol/g mixed oxide) <sup>d</sup>	groups to the ferrocene <sup>d</sup>	Surface area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (Å)	
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> nanosized <sup>a</sup> Si/Al—APTMS Si/Al—APTMS—ferrocene	8.13 12.35	- 3.75 3.03	- - 7.68	- 2.67 2.16	- - 1.37	_ 	498 378 264	0.045 0.031 0.023	36 25 19	

<sup>a</sup> Molar ratio of Si/Al was 60:40, determined from EDX analysis.

<sup>b</sup> Nitrogen was estimated from the elemental analysis. Fe content determined from ICP analysis.

<sup>c</sup> Determined from the N-contents.

<sup>d</sup> Determined from the Fe-content, assume that Fe ions coordinated with aliphatic ligands.

<sup>e</sup> The pore size calculated using the BJH method.

the fact that the CHN content increased with increase in organic chain size, due to the immobilization of organometallic groups (ferrocenecarboxaldehyde) on the  $SiO_2/Al_2O_3$  matrix. The loading of Fe in the heterogeneous FNC was characterized by elemental analyses. The final metal content was 1.37 mmol g<sup>-1</sup>, indicated that 63.4% of the aliphatic ligands were complexed with the ferrocene groups (Table 1).

# 3.1.1. The FTIR spectra

In Fig. 1, the FT-IR spectra of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-APTMS and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-APTMS=ferrocene are shown. The strong absorption bands related to Si-O-Si stretching vibrations are observed in the spectrum of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> at 1010–1290 and 798 cm<sup>-1</sup>. The FT-IR spectrum of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-APTMS shows several signals originating from amino propyl groups, which are related to C-H stretching modes of the propyl, appeared in the area of 1450-1560 and 2935–2860 cm<sup>-1</sup>. It could be concluded from the above results that the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was modified by amine spacer groups successfully. The N–H deformation peak at 1540–1560 cm<sup>-1</sup> confirms the successful functionalization of the Si/Al mixed oxide with 3-APTMS. In Fig. 1A, the C=N imine vibration signal was observed at 1637 cm<sup>-1</sup>, which shows the condensation reaction between ferrocene with organo-functionalised SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The peaks at the 3025-3066 cm<sup>-1</sup> ranges are attributed to the C–H stretching vibrations of ferrocene aromatic rings. The peaks at 1439–1435 cm<sup>-1</sup> can be assigned to C=C stretching vibration of two organic ring systems (cyclopentene groups).

#### 3.1.2. The UV-vis spectra

By comparing the UV-vis spectrum of the  $SiO_2/Al_2O_3$  and the  $SiO_2/Al_2O$ -APTMS=ferrocene (Fig. 2), was observed that the



**Fig. 1.** FTIR spectra of: (A) SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS; and (B) SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene.

UV–vis spectrum of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> had the side-band adsorption near 249 nm but, in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene transitions of  $\mu \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  of the aromatic rings caused strong adsorption in the 260–360 nm .The color of the FNC changed from yellow to red, a characteristic of immobilized Fe ion species, after the reaction with Ferrocenecarboxaldehyde. Furthermore, UV–vis spectra indicated the appearance of several new metal d–d migration bands around  $\lambda$  = 500–700 nm in FNC.

## 3.1.3. SEM, TEM, and EDS

In Figs. 3 and 4 selected images showing scanning electron microscope (SEM), TEM and also size distribution (Fig. 5) of nanoscale SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene are presented. The average particle size in reversed micro emulsion solution was about 24 nm (Figs. 4 and 5). According to the small nanoparticle size and ligand capping as an obstacle in agglomeration, the Fe-nanocatalyst could be used as a suitable catalyst for oxidation of different substrates such as ethylbenzene, cyclohexene and benzyl alcohol. However, the presence of Fe ions in the FNC resulted from the ferrocene groups that purposely coated to increase the electrical conduction and hence to improve the quality of SEM micrograph (Fig. 4).

#### 3.1.4. XPS analysis

The XP spectroscopic analysis of the heterogeneous catalyst was used to study the oxidation state of the active sites of immobilized ferrocene molecules on the surface of nano-scale SiO<sub>2</sub>/Al<sub>2</sub>O (Fig. 6). This technique has previously been shown to provide valuable information regarding the chemical state of the catalytically active sites in different catalysts [49–52]. The XPS spectrum of FNC produced a Fe 2p<sub>3/2</sub> and a Fe 2p<sub>1/2</sub> peak at 711.1 and 724.1 eV, respectively, and are depicted in Fig. 6. However, there is a satellite peak at 715.5 eV beside the main peak of Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> in FNC. These results indicated that most of the Fe ions on the surface



Fig. 2. DR UV-vis spectra of: (A) SiO\_2/Al\_2O\_3; (B) SiO\_2/Al\_2O\_3—APTMS; and (C) SiO\_2/Al\_2O\_3—APTMS=ferrocene.



Fig. 3. SEM of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (left), SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene (right).



Fig. 4. TEM image corresponding to SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene sample.

of the heterogeneous catalyst were in +3 oxidation state (due to the binding energy (BE) of 711.1 and 724.1 eV which are attributed to Fe(III) state of iron) [53]. It is believed that during the immobilization of ferrocene over the modified  $SiO_2/Al_2O_3$  under air condition (in the presence of an atmospheric oxygen) iron oxidation state of ferrocene (Fe(II)) was easily oxidized and began to prefer the Fe(III)



Fig. 5. Particle size distribution of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene.

state (In fact, oxidation of ferrocene gives a stable cation called ferrocenium) [54].

## 3.1.5. Thermal stability

Thermal stability of the synthesize materials were studied with TGA (thermo gravimetric analysis) in Ar atmospheres in the range of 25–1200 °C with a ramping rate of 10 °C/min (Fig. 7). Thermal analysis (TG) of nanoscale SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> showed two stages of weight loss, Stage I (25–115 °C) corresponds to the desorption of physically held water (2.6 wt.%), on the surface of nanoscale SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and Stage II (120–1200 °C) is due to the condensation of Al–OH and Si–OH (13.4 wt.%), which present in the structure of support (for example; 2Si–OH  $\rightarrow$  Si–O–Si + H<sub>2</sub>O). However, NFC showed three distinct steps: at 25–107, 110–625 and 625–1200 °C (Fig. 7). Stage II (110–625 °C) is due to desorption of water molecules from the pores of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and also decomposition of the immobilized organic functional groups (–*pr*-NH<sub>2</sub>). The additional weight losses in Stage III could be observed due to the several phenomena; the



Fig. 6. XP spectroscopy of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene.



Fig. 7. TG curve profiles of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene.

calcination of coke, the loss of the new generated Al—OH and Si—OH groups and decomposition of the immobilized ferrocene group.

From thermogram analysis of samples, it could be concluded that thermal stability of nanoscale  $SiO_2/Al_2O_3$  in NFC improved rather than unmodified  $SiO_2/Al_2O_3$  and the weight losses of the modified  $SiO_2/Al_2O_3$  with ferrocene group in the temperature range of dehydration are less than that for unmodified  $SiO_2/Al_2O_3$ .

#### 3.2. Oxidation of ethylbenzene

To optimize the effectiveness of oxidation condition of ethylbenzene (EB) by TBHP in the presence of nano-Fe-catalyst, various parameters such as the amount of the substrate to oxidant, the temperature, and the nature of the solvent on the performance of the heterogeneous Fe catalyst were investigated. In this reaction major products are acetophenone (1), Benzaldehyde (2) and benzoic acid (3) (Scheme 2). The GC analysis did not show any oxidation products of the aromatic ring in effluents.

In order to study the effect of solvent on the oxidation of EB different solvents such as acetonitrile, ethanol, water, benzene and dichloromethane at 50 °C were experimented (Fig. 8). The reaction at the presence of coordinating solvents such as ethanol had low conversion, while using water as a solvent made no reaction. It seems that the donor electrons of these solvents had more ability to occupy the vacant space around the existed metal in catalyst, so this phenomena could prevents coordinating of Fe active center by oxidant molecules [55]. The major product in oxidation of EB in all solvents was acetophenone. The percentage of EB conversion obtained at different solvents decreased as following; 35.5% (dichloromethane)>27.0% (acetonitrile)>18.0% (ethanol)>0.0% (water). In fact, the use of polar and protic solvents favors selectivity to the production of benzaldehyde and benzoic acid, while the aprotic and chlorinated solvents lead selectivity to



Scheme 2. Reaction products of the catalytic oxidation of ethylbenzene with  $SiO_2/Al_2O_3$ —APTMS=ferrocene.



**Fig. 8.** The influence of solvent on the ethylbenzene oxidation by the  $SiO_2/Al_2O_3$ —APTMS=ferrocene catalyst. *Conditions*: ethylbenzene, 9 mmol; Cat., 50 mg; TBHP, 9 mmol; 24 h; *T*, 50 °C.

acetophenone. It can be seen that acetophenone selectivity is high with a dipolar aprotic solvent in the following order; acetonitrile (74.0%) > dichloromethane (67.8%) > ethanol (29.0%) > water (0.0%). Thus, dipole moment of the solvents probably is an essential factor in oxidation of EB. More investigations showed that the reaction under the solventless condition in comparison with the presence of solvent (like polar and nonpolar) had high selectivity and more catalytic activity (Fig. 8). This shows that the EB and solvent molecules are competitors for the active sites of metal center on the catalyst.

In order to evaluate the effect of substrate/oxidant molar ratio on the catalytic activity and selectivity in solventless condition, the reactions were experimented at different molar ratios of EB:TBHP (1:1, 1:3 and 1:5) at  $50 \,^{\circ}$ C after 24 h (Fig. 9). It was indicated that the different molar ratio of EB:TBHP has strong effects on catalytic activity and selectivity. In most of the experiments acetophenone was the major product, and the best condition was 1:3 molar ratio, due to the presence of excess TBHP coordinated with active sites of the FNC (heterogeneous Fe catalyst) (Fig. 9). In all EB oxidation system, as the reaction time increased, the conversion and selectivity to acetophenone increased as well.

Increasing the temperature for accelerating the reaction is apparently effective. Therefore, the temperature effect ( $50 \circ C$ ,  $80 \circ C$ and  $100 \circ C$ ) was also monitored on the oxidation of EB at the EB:TBHP molar ratio of 1:1 after 24 h in the presence of FNC (Fig. 10). Generally, by increasing reaction temperature and time, the conversion grows higher (87%) and also the selectivity to acetophenone increased (99%) while selectivity to benzaldehyde and benzoic acid decreased. Thus, raising temperature is effective for the oxidation reaction since the energy was not sufficient for the activation of oxygen molecules or the catalytic circulation at low temperature.

To estimate the reusability of FNC, after the first run, the catalyst was filtrated and washed with ether and dried at 80 °C under vacuum and then used for the next run under the same conditions (Fig. 11). No apparent loss of activity and selectivity was observed after 9th run, confirming that FNC has high stability during the catalytic process. To further proof that the oxidation reaction was catalyzed by the heterogeneous Fe-catalyst, we added extra ethylbenzene to the filtrate after the removal of FNC and found that no more products were produced under the same conditions.

To explore the effect of active sites of FNC (Fe centers), oxidation of ethylbenzene was performed by unmodified  $SiO_2/Al_2O_3$  as the catalyst in the presence of TBHP. Consequently, a surprisingly zero level of catalysis was observed under the detection limit of



**Fig. 9.** The influence of different oxidant ratio on the ethylbenzene oxidation by the  $SiO_2/Al_2O_3$ —APTMS=ferrocene catalyst. *Conditions*: ethylbenzene, 9 mmol; Cat., 50 mg; *T*, 50 °C; solventless.

GC. However, the catalytic activity of TBHP toward the oxidation of ethylbenzene in the absence of FNC was investigated and again non product was detected in effluent.

Concerning the catalytic mechanism of FNC, Scheme 3 shows a reasonable proposed mechanism based on the precedent literature for similar Fe(III) catalyst in hydrocarbon oxidation by TBHP [56–58,28]. In first step, Fe(III) active site of the catalyst could coordinate with distant oxygen of TBHP, and *tert*-butylperoxyl radical (t-BuOO•) will be generated that could abstract a hydrogen atom from ethylbenzene and the aryl radical is formed (steps 2 and 3). This observation demonstrates that Fe(III) center is not engaged with the solvent or any other substrate and is free to coordinate with the distant oxygen of oxidant. In the next step, the activated distant oxygen of co-coordinated TBHP reacted with ethylbenzene to yield the products. After that the oxidation reaction might



**Fig. 10.** The influence of reaction temperature on the ethylbenzene oxidation and selectivity to acetophenone by the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene catalyst. *Conditions*: ethylbenzene, 9 mmol; Cat., 50 mg; TBHP, 9 mmol; solventless.

be occurred through competing pathways (steps 4 and 5). In the next steps (1-*tert*-butoxyethyl)benzene could be converted to acetophenone via elimination of *tert*-butanol/water or turnover to benzaldehyde with loosing methanol [26]. In step 8, the (1-*tert*butoxyethyl)benzene is reduced by Fe(II) ions and, that is, Fe(III) active site will be generated again [59–61], and resulting of this step is formation of products.



**Fig. 11.** Reusability of the  $SiO_2/Al_2O_3$ —APTMS=ferrocene on through oxidation of ethylbenzen. *Conditions*: ethylbenzene, 9 mmol; Cat., 50 mg; TBHP, 9 mmol; *T*, 50 °C; solventless.



Scheme 3. Possible pathway for the oxidation of ethylbenzene to acetophenone by SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene in the presence of tert-butyl hydroperoxide.

### 3.3. Oxidation of cyclohexene

To examine the catalytic activity of synthesized catalyst (FNC), oxidation of cyclohexene was carried out under solventless conditions at 120 °C by applying TBHP as oxidant reagent (Scheme 4).

The products of this reaction were 2-cyclohexene-1-one(1), cyclohexene oxide(2), and 1,2-cyclohexandiol(3) which were identified by GC–MS and quantified by GC. The formation of 1-(*tert*-butylperoxy)-2-cyclohexene indicates the presence of radical reactions (data not published) [43,62]. Fig. 12 shows that at same temperature 120 °C, but with different molar ratios of CH:TBHP(1:1 and 1:3) cyclohexene conversion and the selectivity of the products have been changed. Changing the molar ratios of CH:TBHP to (1:3) within 24 h increased the cyclohexene conversion and selectivity to 2-cyclohexene-1-one from 27.7 to 39 and 96.0 to 99.0%, respectively (Fig. 12). Thus, it is obvious to draw the conclusion that under the mentioned reaction conditions, the C=C double bond is less reactive than allylic hydrogen. As we know, allylic radical is the product of the hydrogen abstraction from the allylic carbon, in



**Scheme 4.** Possible products that can be obtained from the oxidation of cyclohexene.

which reaction needs a lower activation energy in comparison with the reaction at double bond [63].

In order to examine the reusability of the immobilized Fecatalyst onto the  $SiO_2/Al_2O_3$ , several successive experiments were carried out by application of the used catalyst (Fig. 13). The results shown that there is no significant loss of activity and selectivity even after 8th run. Therefore, the results clearly proved that under solventless condition FNC catalyze conversion of cyclohexene (87.0%) with ca. 99.0% selectivity to 2-cyclohexene-1-one.

In fact metal ions which catalyze oxygen transfer reactions with TBHP can be separated into two kinds based on the active intermediate: peroxometal or an oxometal complex [64]. Proxometal routes usually possess early transition elements with d<sup>0</sup> configuration, such as Mo(VI), W(VI), V(V) and Ti(IV). However, oxometal routes possess late or first row transition elements, such as, Cr(VI), V(V), Mn(V), Ru(VI), Ru(VIII) and Os(VIII). Some dependent elements on the substrate can involve oxometal or peroxometal routs. Olefin epoxidation and heteroatom oxidations are the reactions that especially involve peroxometal routes. On the other hand, oxometal species display a broader range of activities including allylic oxidations. Also, peroxometal routes do not possess any changes in oxidations state of the metal. However, an oxometal route involves redox reactions of the metal ions after the coordination reaction between reactive oxygen of TBHP with iron, consequently, oxidant activated and conversion of cyclohexene to hydroperoxy-cyclohexene is carried out. Based on the above discussions, a plausible mechanism was proposed for the catalytic oxidation of cyclohexene in the presence of FNC and TBHP as shown



Scheme 5. Proposed mechanism for the oxidation of cyclohexene catalyzed by SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene in the presence of tert-butyl hydroperoxide.

in Scheme 5. At first the FNC needs to be converted to an active form through the interaction with TBHP. Cyclohexene hydroperoxide were produced via the reaction of the Fe<sup>III</sup>-OO-*tert*-Butyl intermediate with cyclohexene. Cyclohexene hydroperoxide has four potential routes in the catalytic oxidation reaction: (1) elimination of water and generation of ketone; (2) redoxe conversion of cyclohexene hydroperoxide into ketone and alcohol; In this step, Fe(III) is reduced to Fe(II) via electron transfer procees; (3) turnovering of cyclohexene to cylohexenepoxide by cyclohexene hydroperoxide as the oxygen source, and (4) conversion of cyclohexene hydroperoxide to alcohol, through transformation of Fe(II) to Fe(III) [56,58,65].

Obviously, to demonstrate the efficiency and effectiveness of catalytic system the obtained results should be compared with other catalytic systems in order to evaluate the benefits and disadvantages of the proposed system. The data are shown in Table 2 show that the catalytic system presented in this paper has the advantages in terms of simple process for the synthesis of

#### Table 2

Comparison of figure of merit of the present work with other studies in the literature for oxidation of ethylbenze and Cyclohexen.

Substrate	Catalyst <sup>a</sup> (amount)	T °C/solvent	Oxidant	Reaction time (h)	Product	Selectivity (%)	[Refs.]
Ethylbenzene	$[Fe(tpa) (MeCN)_2](ClO_4)_2 (5 \mu mol)$	75°C/2-butanone	02	24 h	Acetophenon	54	[66]
	Au/SBA-15, B (15 mg)	70°C/CH₃CN	TBHP	36 h	Acetophenon	93	[67]
	Mn-SBA-15 (0.2 g)	80 °C/−	TBHP	8 h	Acetophenon	53.4	[68]
	TPFPPFeCl (2 mmol)	100°C/-	O <sub>2</sub>	24 h	Acetophenon	82.8	[69]
	CNCr-2 (0.1 g)	70°C/CH₃CN	TBHP	8 h	Acetophenon	69	[73]
	Fe/MgO, NHPI (6 wt%, 20 mol%)	25°C/-	O <sub>2</sub>	20 h	Acetophenon	52	[69]
	Fe (salen)-POM	80 °C/CH₃CN	$H_2O_2$	5 h	Acetophenon	100	[70]
	This work	50°C/-	TBHP	24 h	Acetophenon	89	
Cyclohexene	[Fe (tpa) (MeCN) <sub>2</sub> ] (ClO <sub>4</sub> ) <sub>2</sub> (5 µmol)	25°C/acetone	O <sub>2</sub>	24 h	2-Cyclohexen-1-one	64	[66]
	FePcS-SiO <sub>2</sub> (0.5 mol%)Fe(III) (5,10,15,20-tetrakis)	40 °C/CH₃CN	TBHP	3 h	2-Cyclohexen-1-one	43	[70]
	(pentafluorophenyl) (prophirin) Cl (56 μg)	50 °C/−	02	2 h	2-Cyclohexen-1-one	64	[71]
	LFe <sup>III</sup> Cl (0.1 mol%)	80°C/CH₃CN	$H_2O_2$	4 h	2-cyclohexen-1-one	30	[72]
	LFe <sup>III</sup> SiO <sub>2</sub> (0.1 mol%)	80°C/CH₃CN	$H_2O_2$	24 h	2-Cyclohexen-1-one	44.7	[73]
	MnTPPCl-Co(OAc) <sub>2</sub> ( $6 \times 10^{-5}$ )	80°C/CH₃CN	O <sub>2</sub>	12 h	2-Cyclohexen-1-one	60	[74]
	polymer anchored Cu(II) (0.03 g)	r.t-/H <sub>2</sub> O	TBHP	8 h	2-Cyclohexen-1-one	64	[75]
	ZrP·Fe(Salen) (0.066 g) 80 °C/Benzene	80°C/Benzen	TBH P (70%)	5 h	2-Cyclohexen-1-one	66.34	[76]
	ZrP·Fe(Salen) (0.066 g) 80 °C/Benzene	80°C/Benzen	TBHP (dry)	5 h	2-Cyclohexen-1-one	74.62	[76]
	This work	'120 °C/−	ТВНР	24 h	2-Cyclohexen-1-one	96	

<sup>a</sup> TPFPPFeCl:Fe (5,10,15,20-tetrakis (pentafluorophenyl)) porphyrin, CNCr-2:Nickel substituted copper chromite spinels, NHPI: N-Hydroxyphthalimide, POM: a kegging type polyoxometalate (K<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub>), FePcS-SiO<sub>2</sub>: Fe tetrasulfocyanine was immobilized on SiO<sub>2</sub>, L: (LFeIII·SiO<sub>2</sub>) [L=3-{2-[2-(3-hydroxy-1,3-diphenylallylideneamino)- ethylamino]-ethylimino]-1,3-diphenyl-propen-1-ol], ZrP·Fe(Salen): Iron(III)-Salen intercalated -zirconium phosphate.



**Fig. 12.** The influence of different oxidant ratio on the cyclohexene oxidation by the  $SiO_2/Al_2O_3$ —APTMS=ferrocene catalyst. *Conditions*: cyclohexene, 9 mmol; Cat., 50 mg; *T*, 120 °C; solventless.

nano-catalyst, heterogeneous nature of catalyst (easy separation from the reaction mixture by simple filtration), use of the commercially available molecule FCA as the one of the important starting materials for the synthesis of Fe nano-catalyst, chemical and thermal stability of catalyst, mild condition reaction in the absence of additives and solvent, high conversion and selectively and widely used in catalytic oxidation reactions (ethylbenzene, cyclohexene and benzyl alcohol as substrates), therefore this protocol is very suitable for practical organic synthesis.



**Fig. 13.** Reusability of the  $SiO_2/Al_2O_3$ —APTMS=ferrocene on the oxidation of cyclohexene and selectivity to 2-cyclohexene-1-one. *Conditions*: cyclohexene, 9 mmol; Cat., 50 mg; TBHP, 9 mmol; 24 h;7, 120 °C; solventless.



**Scheme 6.** oxidation of benzyl alcohol to benzyl aldehyde catalyzed by SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>—APTMS=ferrocene in the presence of *tert*-butyl hydroproxid.

able 3
xidation of benzyl alcohol with heterogeneous Fe nano-catalyst

Catalyst	T°C	Conversion (mol%)	Selectivity (mol%) (benzaldehyde)
FNC	25	4.6	100
FNC	40	13.3	100
FNC	60	38.8	100
FNC	80	64.2	100
FNC	100	84.4	100
FNC <sup>a</sup>	100	98.5	100
FNC <sup>b</sup>	100	100	100
FNC <sup>c</sup>	100	84.4	100
FNC <sup>d</sup>	100	84.6	100
FNC <sup>e</sup>	100	84.2	100
FNC <sup>f</sup>	100	84.5	100

Reaction conditions: 1 mmol benzyl alcohol; 1 mmol TBHP; 0.03 g catalyst; 8 h; without solvent.

<sup>a</sup> Benzyl alcohol: TBHP (1:2).

<sup>b</sup> Benzyl alcohol: TBHP (1:2) after 24 h.

c Second run.

<sup>d</sup> Third run.

<sup>e</sup> Fourth run.

<sup>f</sup> Fifth run.

## 3.4. Oxidation of benzyl alcohol

The liquid-phase oxidation of benzyl alcohol was performed by TBHP at 25, 40, 60, 80 and 100 °C over immobilized FNC under different conditions without the use of any solvent (Scheme 6).

Table 3 confirms the highness of catalytic activity and excellent selectivity to benzaldehyde (100%) in all experimental condition. GC analysis showed that benzaldehyde was the sole product (confirmed by performing three replicate experiments). With increasing the temperature from 25 to  $100^{\circ}$ C, the benzyl alcohol conversion increased. However, by reusing the catalyst, the percentage of benzyl alcohol conversion and benzaldehyde selectivity (and therefore, benzaldehyde yield) was constant after fifth times. The nature of the recovered catalyst after reusing three times had been followed by FTIR spectrum, and no significant changes could be seen. Therefore, the heterogeneous nano-iron catalyst with high catalytic activity and stability for the selective oxidation of benzyl alcohol was developed by covalently anchored on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nanoparticles.

# 4. Conclusion

In this study, a novel and simple catalysis system of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nanosized-anchored ferrocenecarboxaldehyde in the oxidation of ethylbenzene, cyclohexene, and benzyl alcohol with TBHP have been used. This catalytic system has some advantages included supplying form cheap raw material, commercially available reagents and is reusable for oxidation of ethylbenzen, cyclohexene and benzylalcohol. Oxidation of alkyl aromatic, allylic site and double bond were resulted with the oxidant of TBHP without the use of any solvent. Under optimum reaction conditions such as substrate/TBHP (1:1), absence of solvent, temperatures of 50–120 °C and reaction time of 24 h, Fe-nano-catalyst showed higher ethylbenzene, cyclohexene, and benzyl alcohol conversion (>84%) and more than 90%

selectivity to acetophenone, 2-cyclohexene-1-one and banzaldehyde, respectively. The cycle usage test indicated that the catalyst prepared by this method was relatively stable after several run. Finally, the felicitous combination of optimal conditions, catalyst design, a highly available catalytic activity and selectivity toward major products should lead to widespread applicability of catalysts such heterogeneous ferrocene.

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