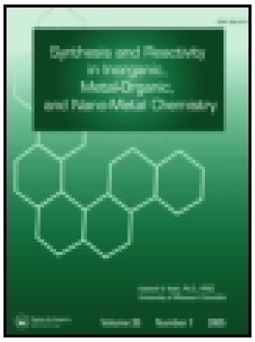

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Nano-Rods of $FeVO_4$: an Efficient Heterogeneous Catalyst for Chemo-Selective Oxidation of Benzylic Alcohols

Akbar Heydari,*[1] Mehdi Sheykhan,[2] Masoud Sadeghi[1] and Iman Radfar[1]

[1] *Chemistry Department, Tarbiat Modares University, P.O. Box14155-4838 Tehran, Iran*

[*] *Corresponding author. E-mail: heydar_a@modares.ac.ir*

[2] *Chemistry Department, University of Guilan, P.O. Box 41335-1914 Rasht, Iran*

Abstract

Controllable fabrication of iron vanadate (FeVO4) was achieved by the hydrothermal approach. The excellent catalytic activity of the prepared nano-rods of iron vanadate for the oxidation of benzylic alcohols as well as its potential for oxidation of the benzylic sp3 C-Hs in the presence of urea hydrogen peroxide (UHP) as oxidant was reported. The prepared nano-rods and nano-spheres were fully characterized by FT-IR, XRD, EDAX, ICP-AES, SEM and TEM. In the presence of the catalyst, alcohols *chemo-selectively* (100%) convert to the corresponding aldehydes/ketones, giving a total turnover number about 380 for ten consecutive runs.

Keywords

Selective oxidation; Heterogeneous catalysis; Iron vanadate; UHP

Introduction

Obviously, chemo-selective oxidation of alcohols to aldehydes and ketones is a crucial transformation in organic chemistry for the synthesis of chemicals of industrial interest [1-7]. Traditional methods for oxidation of alcohols largely consisted of the use of chlorinated solvents and exploiting either Cr(VI) or Mn(VII) reagents affording harsh conditions that restricted using other functional groups within the molecule [4,8] and generate large amounts of toxic waste when used on an industrial scale [8a]. Hence, utilizing milder approaches are always in demand. The other problem that should be tackled about oxidizing agents is the environmental issues. To date, even with newer achievements in utilizing hypervalent iodine reagents, the environmental concerns have not been satisfied yet [9]. These concerns motivated chemists to take advantage of greener methods such as free- or green solvent systems and green or less poisonous reagents and catalysts [10-31]. In this regard, use of environmentally-benign hydrogen peroxide, which leaves water behind at the end of reaction as the only by-product, has taken up a special position as a green oxidant [31-32].

Shi and co-workers reported a heterogeneous nano-Fe(III) oxide catalyzed oxidation of naphthalene derivatives using hydrogen peroxide which benefited from fenton process.33 In addition, it is known that Fenton-like transformations of V(V) to V(IV) participate in the vast majority of the vanadium-induced intracellular events [34-35]. Metal orthovanadates (MVO_4) are an interesting class of compounds with diverse applications in various fields such as solar cells, gas sensors, cathode in lithium batteries and more importantly as catalysts [36-41]. To our knowledge, studies on Fe-V nanocatalysts in selective oxidation of alcohols have been rarely reported. Because of the development of several catalysts through introduction of the transition metals into the iron oxide structure in activation of hydrogen peroxide [42-43] as well as the abilities of Fe(III) and V(V), two ingredients of the 'iron vanadate; $FeVO_4$', in promotion of Fenton process [44], we decided to use iron vanadate as the catalyst of choice. Hence, nanoparticles of $FeVO_4$ with different morphologies were prepared and the prepared catalysts were tested in the oxidation of benzyl alcohol derivatives. It was found that the size of our catalyst has a great effect on its catalytic activity but in the case of morphology it does not matter.

Results and discussion

There are several well-established records for the synthesis of $FeVO_4$ such as heating equimolar of Fe_2O_3 and V_2O_5 at 600 °C [45], wet chemical synthesis via ferric nitrate ($Fe(NO_3)_3$) and ammonium methavanadate (NH_4VO_3) [46], co-precipitation method using $Fe(NO_3)_3.9H_2O$ and NH_4VO_3 in the presence of NaOH [47] and porous $FeVO_4$ nanorods and nanoparticles via hydrothermal synthesis [48].

Nanospheres of $FeVO_4$ **1** and nanorods of $FeVO_4$ **2** were prepared according to the Ref [48]. The prepared nano-materials were fully characterized by XRD (Figure 1), SEM (Figure 2), TEM (Figure 3), EDAX (Figure 4a), ICP, and FTIR (Figure 4b). Diffraction peaks at 10.1°, 11.4 °, 13.8 °, 14.2 °, 16.6 °, 17.5 °, 19.9 °, 20.8 °, 22.9 °, 23.3 °, 25.2 °, 25.8 °, 26.8 °, 27.1 °, 31.3 °, 41.0 ° corresponding to the (001), (010), (0-11), (100), (011), (-111), (101), (-102), (020), (0-21), (012), (-121), (021), (-201), (-122) and (-132) are readily recognized from the XRD pattern. The observed diffraction peaks agree well with the triclinic structure of iron vanadate (JCPDS card no: 38-1372). No other phase except the iron vanadate is detectable.

The morphologies of the catalysts **1** (Figure 2a-b) and **2** (2c-d) were proved by SEM. As it is clear, the catalyst **1** has a sphere-like morphology but in the case of the catalyst **2** the little nanorods are detectable. The obtained histogram (Figure 2e-f) confirmed the fact that the size of distribution for 50 observed nanospheres and nanorods was a narrow normal one with an average value of 81 nm and 305 nm × 2.5 µm, respectively.

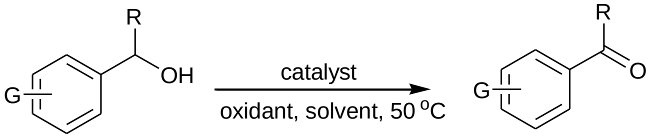
Figure 3 shows the typical TEM images of nanospheres **1** (a-d) and nanorods **2** (e-h) prepared by the hydrothermal reaction. As can be seen from the image, the average diameter of the as-synthesized nanospheres and nanorods were about 70 nm and 150 nm × 1.3 µm, respectively. TEM images prove the prepared nanoparticles have good dispersibility in size and shape.

To confirm the presence of iron and vanadium elements, the energy-dispersive X-ray spectroscopy (EDAX) was used. As is illustrated in Figure 4a, elemental analysis of $FeVO_4$ nanoparticles by means of EDAX spectroscopy shows Fe and V elements in the prepared structures. The quantitative analysis by using EDAX proved the presence of Fe and V at 31.2 and 29.6 % as expected.

Verifying the results obtained by EDAX is carried by the Inductive Coupled Plasma-Atomic Emmission Spectroscopy (ICP-AES). The analysis showed 32.5 % Fe and 29.3% V in the structure of the prepared nanoparticles.

In FTIR (Figure 4b), characteristic absorption bands due to the V-O terminal stretching appeared at 964, 925 and 887 cm^{-1} while bridging V-O---Fe stretching can be seen at 740 and 694 cm^{-1}. Additionally, V-O-V deformation was observed at 516 cm^{-1} [49].

The efficiency of iron vanadate nanorods was initially investigated in the oxidation of benzyl alcohol as a model reaction. Reaction conditions such as solvent, temperature, oxidant, mole percent and morphology of the catalyst were optimized as is shown in Table 1.



It was found that starting from benzyl alcohol, 2 mol% of catalyst **2**, 2.5 equivalent of UHP as oxidant, 2 mL of acetonitrile as solvent at 50 °C led to the formation of benzaldehyde in 82% yield and 100% selectivity (entries 1-12). Compared to $FeVO_4$ in bulk, nano forms had better function (entries 13,14). The results showed no marked difference when $FeVO_4$ was exploited in the forms of either nanospheres **1** or nanorods **2**. Diversity of the reaction was investigated by using the catalyst **2** proving that under the similar reaction conditions it is a highly efficient and selective heterogeneous catalyst for the oxidation of a wide range of primary and secondary benzylic alcohols (Table 2).

The oxidation of hydrocarbons to more functional compounds is one of the most important processes in petrochemical transformation which were previously operated with various catalytic processes using catalysts such as Ru(III) and oxidants such as hypervalent iodine and oxone [50-52]. However, these methods have some disadvantages such as leaching of iron ion, necessity of separation of iron ions at the end of the reaction, limited pH range applicable (pH=2-3) and deactivation of the catalyst due to the formation of a complex between iron ions and anions present in the reaction media [53]. Recently, Zhang et al. have developed a novel heterogeneous Pd catalyzed aerobic oxidation of hydrocarbons [54]. Although it was an outstanding breakthrough, efforts to increase the reaction conversion is still of great importance. To highlight the aptitude of the catalyst prepared, we tested the oxidation of sp^3 C-H bond of indane using our catalyst. Oxidation of indane provided good results (Scheme 1). In fact, it was selectively oxidized to 1-indanone while oxidation to indan-1-ol, 1-H-indene or hydroperoxy compound did not occur. In addition, the blank oxidation (in the absence of the catalyst) gave no conversions.

Noticeably, the result was promising indicating potential of the catalyst in these kinds of reactions: selective oxidation of alkyl aromatic compounds to aromatic ketones.

The most liked mechanism of Fe(III) and V(V) participations in Fenton-like reaction is to activate hydrogen peroxide as the following reactions [44, 55-56] (Scheme 2):

Hence the above processes were proved by different methods [44], the reaction mechanism should be related to the production of free radical OH. We propose that after the production of hydroxyl radical (as shown in scheme 2 attributed to either the catalytic mechanism involved in the Fe(III)/Fe(II) or V(V)/V(IV) redox couples), it abstracts a hydrogen atom from the alcohol to form an alcohol-radical species that subsequently undergoes a terminative reaction with another hydroxyl radical and then an α-elimination to give aldehyde and water (Scheme 3).

Ruling out the deactivation (caused by the leaching/sintering) of a heterogeneous catalyst is within issues that matters and must be scrutinized. The heterogeneous nature of the catalyst was confirmed when the reaction mixture of entry 1 in Table 2 was filtered after 20 min (15% conversion). The catalytic activity was suppressed in the filtrate during 8 h after filtration. To show that no deactivation occurred in the oxidation of benzyl alcohol (Table 2, entry 1), the recovered catalyst was successively used in a second run. Setting the reaction time to 2 h, comparably good yields of benzaldehyde were obtained in 10 subsequent runs using the same catalyst to give a total turnover number (TON) about 380.

Conclusion

In summary, a promising *fenton-like catalyst* for oxidation of benzylic alcohols as well as benzylic C-H bonds was introduced by use of nanorods and nanospheres of $FeVO_4$. Under the foregoing conditions, the reactions of the alcohols chemo-selectively (>98% to 100%) led to the corresponding aldehydes/ketones, mainly due to the mild reaction conditions. In addition to compatibility with green chemistry, $FeVO_4$-H_2O_2 revealed some advantages than does precedent catalysts (like iron oxide) for benzylic alcohol oxidation including (i) being free from leaching, (ii) having applicable pH in which the reaction can be conducted (pH=3-8 for $FeVO_4$ in comparison with pH=2-3 for iron oxide) and (iii) not forming a complex between iron ion and available anions in solution.

Experimental

Preparation of nanorods and nanospheres of $FeVO_4$ [48]

All of the chemical reagents were in analytical grade. For typical synthesis of $FeVO_4$ nanorods, 10 mL of 0.3 mol.L^{-1} ammonium methavanadate (NH_4VO_3) was added to 10 mL 0.3 mol.L^{-1} ferric nitrate ($Fe(NO_3)_3$) under stirring. Orange precipitation formed was transferred to the autoclave, heated at 180 ^oC for 3 h and then allowed to cool down to room temperature. The $FeVO_4.1.1H_2O$ formed was collected by centrifuge and washed with deionized water and ethanol several times. The product was then vacuum-dried at 60 ^oC for 6 h. The $FeVO_4$ nanorods were obtained by calcination of $FeVO_4$ prepared in a furnace at 550 ^oC for 24 h.

To prepare $FeVO_4$ nanospheres, the same procedure was adopted using less concentration (0.01 mol.L^{-1}) of precursors (iron vanadate and ammonium methavanadate).

General procedure for catalytic oxidation of benzylic alcohols

Alcohol (1 mmol) and 2 mol% of catalyst were added to a glass reactor and stirred at 50 °C for 3 h during which either hydrogen peroxide (30%, 0.2 mL, 2.5 equiv.) or urea hydrogen peroxide (2.5 equiv.) was continuously added. The progress was monitored by TLC. Ultimately, the catalyst was separated by filtration, washed with diethyl ether and dried to be reused in the next run. All isolated products gave satisfactory spectral data [57].

General procedure for benzylic C-H oxidation

Substrate (1mmol) and 2 mol% of $FeVO_4$ nanorods were added to a glass reactor containing acetonitrile as solvent (2 mL). Hydrogen peroxide (30%, 0.2 mL, 2.5 equiv.) was added and the above-mentioned mixture was allowed to be stirred at 80 °C for 12 h. The catalyst was separated by filtration, washed with diethyl ether and dried to be reused in the next run. The isolated product gave satisfactory spectral data. The reaction was also implemented using urea hydrogen peroxide (2.5 equiv.) under the same conditions giving rise to the similar results detected by TLC.

Acknowledgement

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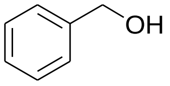
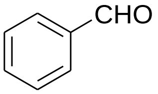
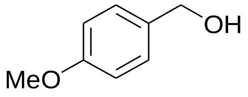
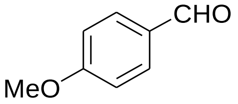
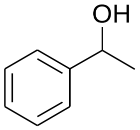
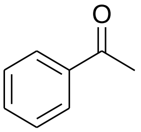
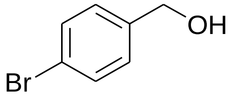
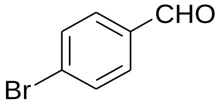
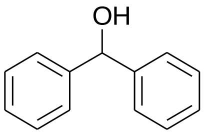
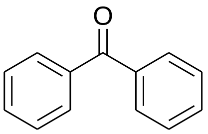
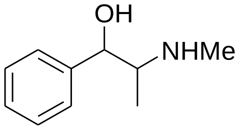
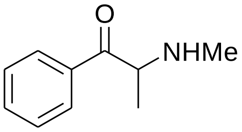
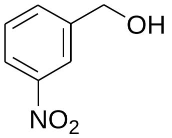
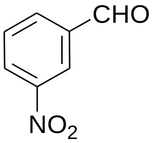
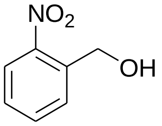
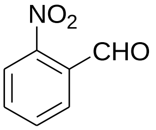
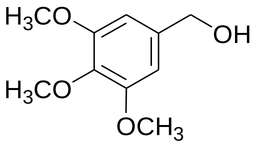
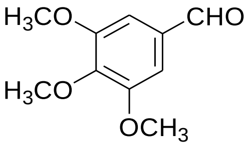
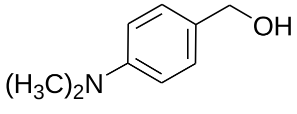
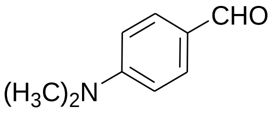
Table 1. Solvent, catalyst and oxidant screening for the oxidation of benzyl alcohol[a]

entry	catalyst mol%	oxidant	solvent	t (h)	yield (%)[b]	selectivity (%)[c]
1	0.5	H_2O_2	DCE	5	29	77
2	1	H_2O_2	DCE	5	35	72
3	2	H_2O_2	DCE	5	43	80
4	2	H_2O_2	ACN	5	77	94
5	2	H_2O_2	DCM	5	48	85
6	2	H_2O_2	Toluene	5	trace	n.d.[d]
7	2	H_2O_2	H_2O	5	44	74
8	2	H_2O_2	solvent free	5	69	89
9	2	H_2O_2	ACN	1	48	n.d.[d]
10	2	H_2O_2	ACN	2	65	n.d.[d]
11	**2**	**H_2O_2**	**ACN**	**3**	**74**	**96**
12[e]	**2**	**UHP**	**ACN**	**3**	**82**	**100**
13[f]	2	UHP	ACN	10	29	n.d.[d]
14[g]	2	H_2O_2	ACN	3	72	95
15[h]	2	H_2O_2	ACN	3	56	90
16[i]	**2**	**UHP**	**ACN**	**3**	**80**	**>98**

[a] Unless otherwise stated, reactions were performed on a 1 mmol scale of benzyl alcohol using 2.5 equiv. H_2O_2 in the presence of catalyst **2** at 50 ^{o}C in 2 mL solvent. [b] Yields of isolated products. [c] Determined by flash chromatography as the ratio of (benzaldehyde)/(benzaldehyde+benzoic acid). [d] not determined. [e] 2.5 equiv. UHP was used. [f] 0.5 equiv. UHP was used. [g] Catalyst **1** was used. [h] Bulk $FeVO_4$ was used. [i] The reaction was performed on a scale of 10.0 mmol benzyl alcohol.

Table 2. Chemo-selective oxidation of benzylic alcohols via $FeVO_4$ nanorods [a]

entry	substrate	product	Obs. m.p. (°C)	Yield	TON[b]	TOF[c] (h^{-1})	Selectivity (%)
1[d]			-	82	41(>380[e])	13.7	100
2			-	85	42	14	100
3			-	72	36	12	100
4			54-55	78	39	13	100
5			45-47	75	37	12.3	100
6			-	80	40	13.3	100
7			57-60	77	38	12.7	100
8			41-43	75	37	12.3	>98[f]
9			71-73	84	42	14	100
10			69-72	87	43	14.3	100

[a] As the procedure described in experimental section. [b] [reacted moles of alcohol/total moles of catalyst]. [c] [TON/reaction time (h)]. [d] The catalyst was reused 10 times. [e] Total turnover number of 10 experiment. [f] Determined by flash chromatography as the ratio of (aldehyde)/(aldehyde+carboxylic acid).

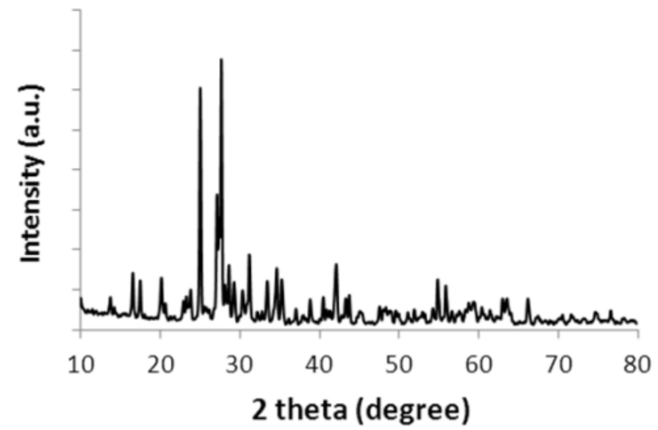


Figure 1. X-ray diffraction spectroscopy of the catalyst **2**

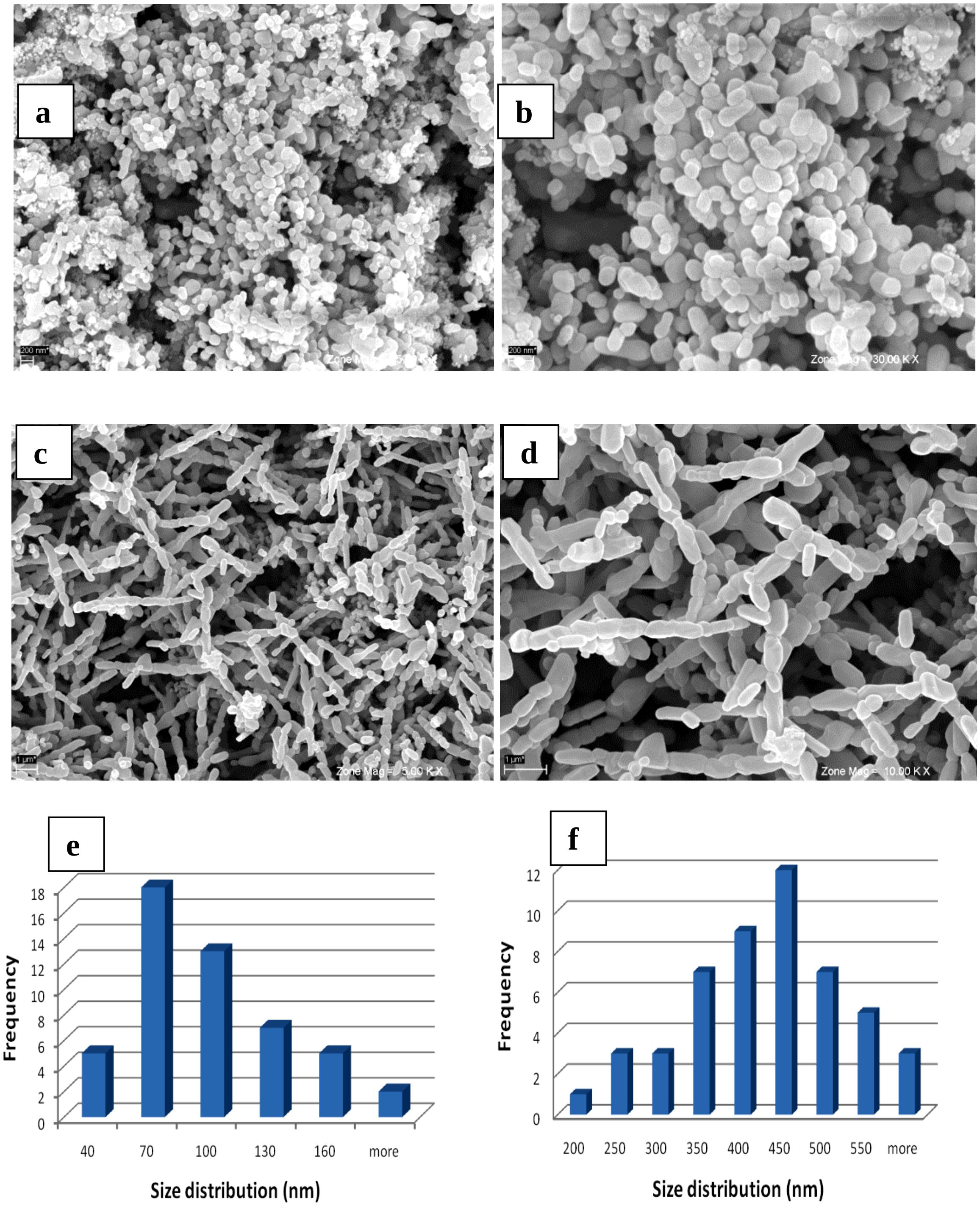
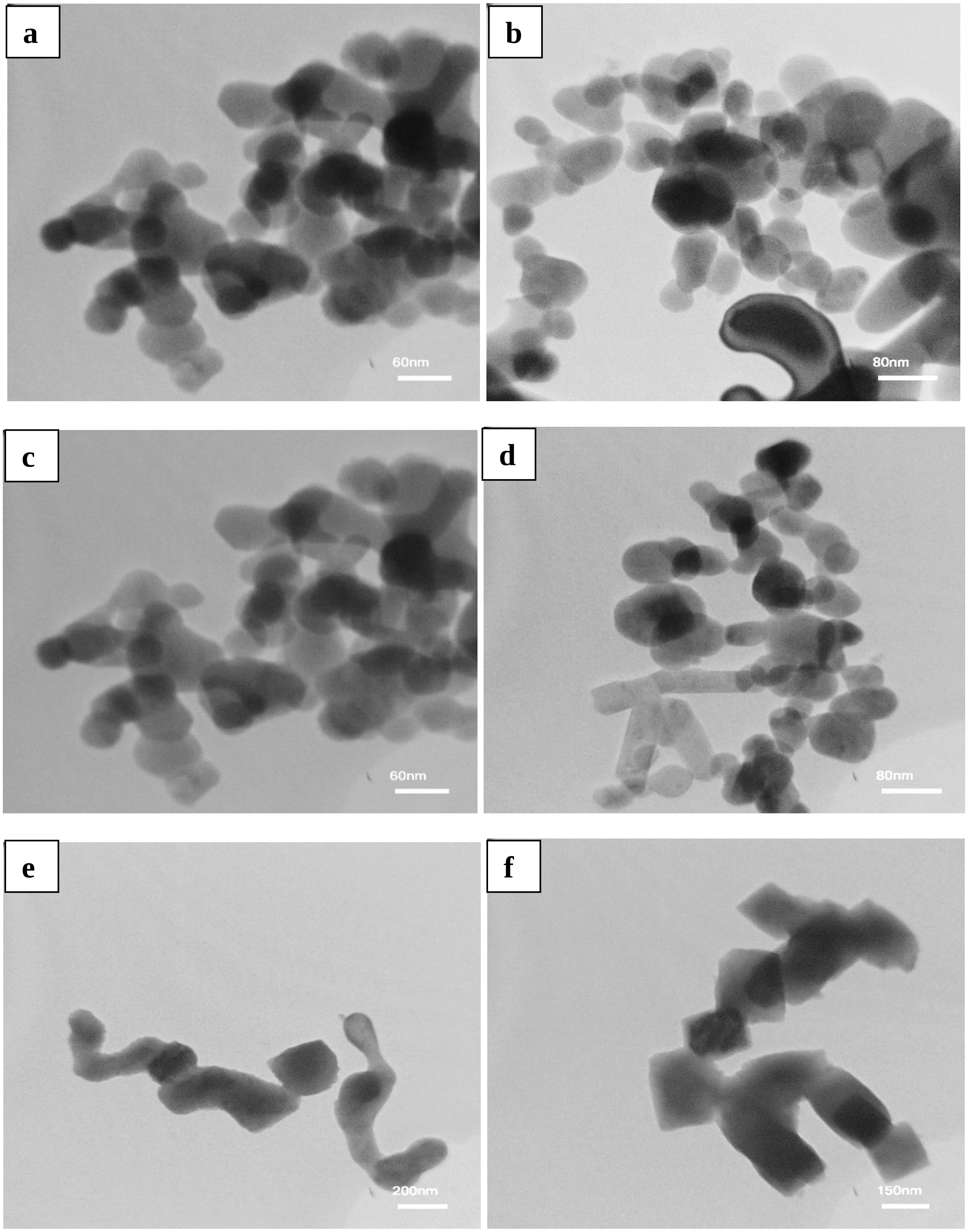


Figure 2. SEM photographs of catalyst **1** (a-b) and catalyst **2** (c-d), statistical analysis of catalyst **1** (e) and catalyst **2** (f)


a
60nm
b
80nm
c
60nm
d
80nm
e
200nm
f
150nm

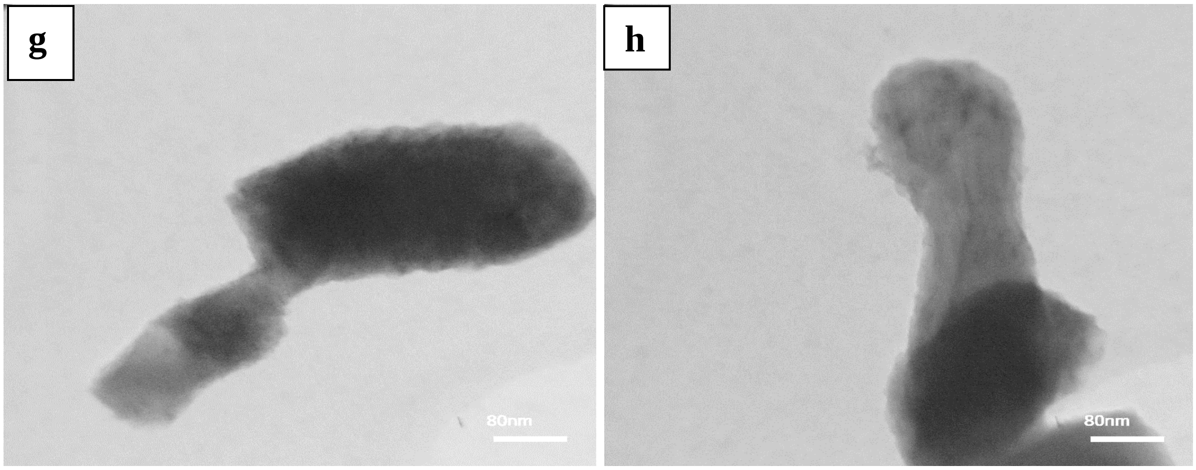


Figure 3. TEM images of catalyst **1** (a-d) and catalyst **2** (e-h)

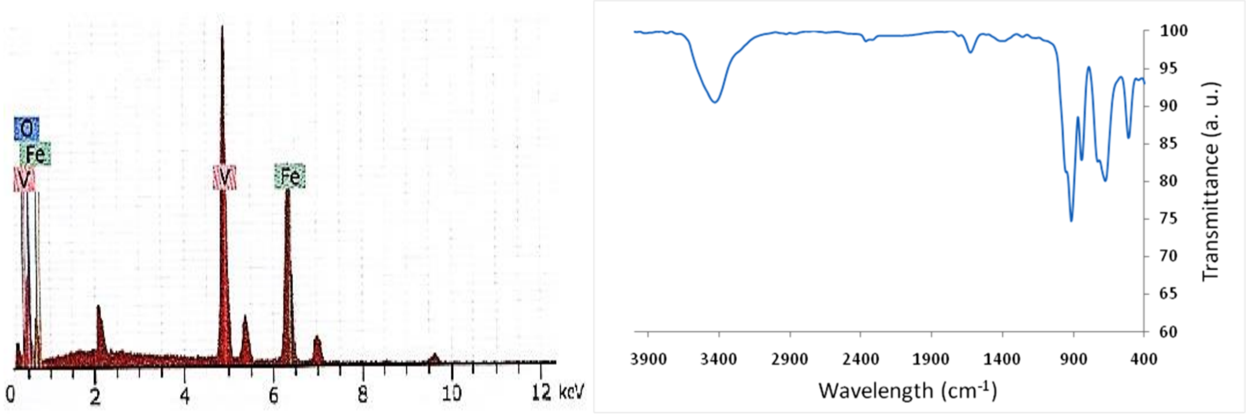
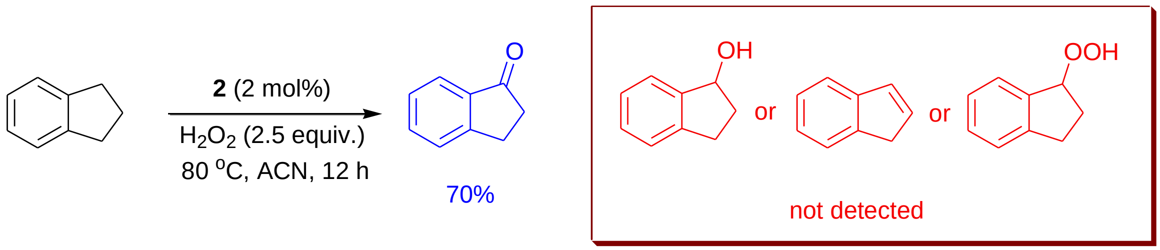


Figure 4. Energy-dispersive X-ray spectroscopy (EDAX) (a) and FTIR (b) of catalyst **2**



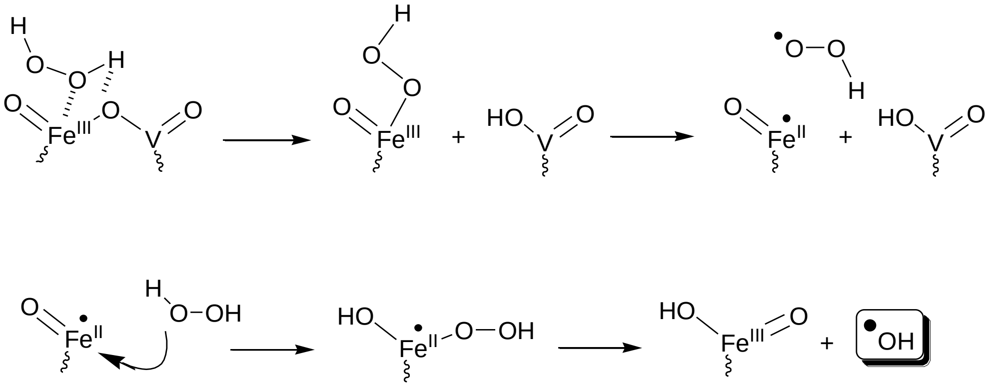
Scheme 1. Catalytic oxidation of *sp*^{3} C-H bond

$$\mathrm{Fe^{III}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe^{II}} + {}^{\bullet}\mathrm{OOH} + \mathrm{H^{\oplus}}$$

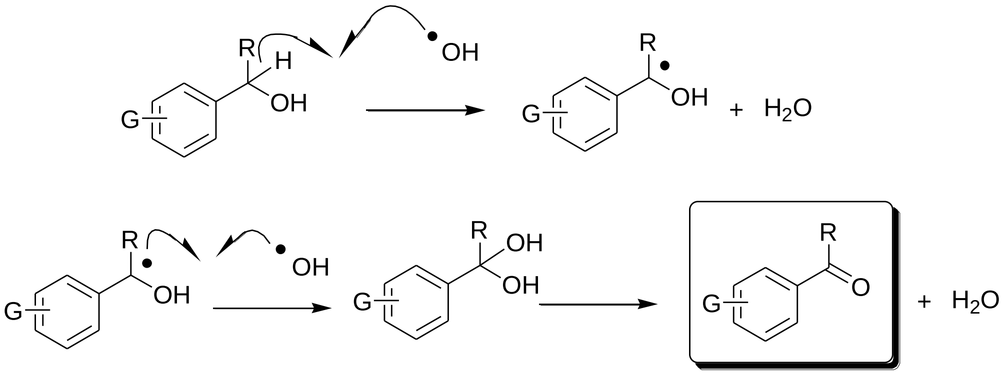
$$\mathrm{Fe^{II}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe^{III}} + {}^{\bullet}\mathrm{OH} + \mathrm{HO^{\ominus}}$$

$$\mathrm{V^{V}} + \mathrm{H_2O_2} \longrightarrow \mathrm{V^{IV}} + {}^{\bullet}\mathrm{OOH} + \mathrm{H^{\oplus}}$$

$$\mathrm{V^{IV}} + \mathrm{H_2O_2} \longrightarrow \mathrm{V^{V}} + {}^{\bullet}\mathrm{OH} + \mathrm{HO^{\ominus}}$$



Scheme 2. Proposed simplified mechanism for decomposition of one hydrogen peroxide molecule by a Fe-O-V moiety in iron vanadate



Scheme 3. Proposed mechanism for the oxidation of alcohols by the $FeVO_4$-H_2O_2 catalyst