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REGULAR ARTICLE

One-pot three-component synthesis of 1,8-dioxooctahydroxanthenes and 14-Aryl-14Hdibenzo[*a,j*]xanthenes using a new nanostructure zeolite

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Abstract. A new modified zeolite containing Fe nanoparticles loaded in zeolite X (Fe-X) has been synthesized and characterized by FT-IR, XRD, EDX and SEM techniques and its catalytic activity has been investigated in the synthesis of two series of xanthene derivatives. We have described an efficient and novel method using Fe-X as a new and reusable catalyst for the synthesis of 1,8-dioxooctahydroxanthenes and 14-aryl-14H-dibenzo[*a,j*]xanthenes derivatives from one-pot three-component condensation of aromatic aldehyde and dimedone or β-naphthol under solvent-free conditions. The significant advantages of the present method are high yields of products, short reaction time, easy separation of the catalyst from the reaction mixture, easy product isolation, solvent-free condition and reusability of the catalyst.

Keywords. Nanostructure zeolite X; one-pot synthesis; 1,8-dioxooctahydroxanthene; 14-aryl-14H-dibenzo[*a,j*]xanthene.

1. Introduction

Zeolites are hydrated aluminosilicate frames based on an extremely large three-dimensional network of AlO_4 and SiO_4 tetrahedral that are linked together by oxygen atoms. The exceptional properties of zeolites include ion exchange capability, thermal stability and recyclability. Furthermore, they have been applied as catalyst in the petroleum refining and industrial processes.[1–3] The basic formula of zeolites can be represented as: $M_{x/n}[(Al_2O_3)_x(SiO_2)_y]wH_2O$ where, M is the alkaline or alkaline earth metal. Structurally, zeolites contain small cavities like alkaline and alkaline earth metal cations in a non-framework position such as sodium, potassium, magnesium, calcium, strontium and barium that can be replaced by transition metals *via* ion exchange process.[4] Zeolites with transition metal ions have the potential to show novel catalytic behavior as these cations are coordinately unsaturated, possess variable oxidation states and can form complexes with guest molecules more selectively than filled shell cations such as Na.[5,6] Zeolite X has an aluminosilicate framework analogous to the naturally occurring mineral faujasite including sodalite cages and a 12-membered ring inner cavity which is surrounded by sodalite cages.[7]

Xanthene derivatives are known as an important class of O-containing heterocyclic compounds that received considerable attention as they have a wide range of valuable biological and pharmaceutical properties such as antibacterial,[8] antiviral,[9] anti-inflammatory,[10] anti-depressants and antimalarial activities.[11] These compounds have been also found to be as antagonists for paralyzing action of zoxazolamine.[12] As well as, these compounds can be used as dyes,[13] in laser technology,[14] photodynamic therapy,[15] pH-sensitive fluorescent materials for the visualization of biomolecules assemblies.[16] In recent years, many different methods have been reported for the synthesis of xanthene derivatives *via* three-component reaction promoted by various catalysts such as silica chloride,[17] alum,[18] p-dodecylbenzenesulfonic acid,[19] cyanuric chloride,[20] $FeCl_3/SiO_2$,[21] $SbCl_3/SiO_2$,[22] $HClO_4/SiO_2$,[23] sulfamic acid-ionic liquid,[24] iodine,[25] $ZrO(OTf)_2$,[26] selectfluor™,[27] $KAl(SO_4)_2.12H_2O_2$,[28] silica sulfuric acid[29] and so on. Although some of the

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procedures reported for the synthesis of these heterocyclic compounds are valuable, most of them have problems such as moderate yields of products, long reaction times, harsh reaction conditions, the use of toxic organic solvents and expensive catalyst.

Therefore, we now wish to report a simple and efficient method for the synthesis of xanthene derivatives *via* one-pot three-component reaction of aromatic aldehyde and dimedone or β-naphthol using a novel nanostructure zeolite X (Fe-X) as an efficient, reusable and non-toxic catalyst.

2. Experimental

2.1 *General information*

All materials were prepared from Merck or Fluka Company. The IR spectra of the compounds were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). ^{1}H NMR and ^{13}C NMR data were obtained using a Bruker AVANCE 300 MHz. A Bamstead Electrothermal apparatus was used to measure the melting points and was uncorrected. The structure of Fe-NaX zeolite was determined using a Holland Philips Xpert X-ray powder diffraction (XRD). Analysis of elemental content of the catalyst was determined by energy dispersive X ray spectroscopy (EDX) model MIRA III. The morphology of Fe-NaX and size of nano-particles were determined by scanning electron microscopy (SEM) model MIRA III.

2.2 *Catalyst preparation*

First, $FeCl_2.6H_2O$ (1.5 g) was dissolved in 100 mL distilled water and zeolite X (3 g) was added and then stirred at 50 °C for 24 h. After that, the precipitate was filtered. Then distilled water (100 mL) was added to the separated precipitate and the reaction mixture was stirred at room temperature and during stirring, hydrazine was added. Then, the obtained product was filtered and washed with distilled water and dried in oven for 3 h at 150 °C. For complete reduction of iron ions, the obtained precipitate containing iron particles was dissolved in distilled water (100 mL), and stirring at room temperature and then a solution of $NaBH_4$ (0.3 g) in distilled water was added dropwise to the mixture. After 30 min the reaction mixture was filtered and dried in oven for 4 h at 150 °C.

2.3 *General procedure for the preparation of xanthens derivatives*

A mixture of dimedone **1a** (2 mmol) or β-naphthol **1b** (2 mmol), aromatic aldehyde **2** (1 mmol) and Fe-X (25 mg) was prepared and heated at 90 °C under solvent-free condition. After the completion of the reaction as monitored by TLC (*n*-hexane/EtOAc, 3:1), hot ethanol (10 mL) was added to the reaction mixture and filtrated for catalyst separation. Then the catalyst washed with ethanol and dried at 120 °C for 2 h. The reaction mixture was cooled to room temperature and the obtained precipitate was filtered and washed with ethanol. Further purification was down by recrystallization in ethanol (Table 2).

2.4 *Physical and spectral data of products*

2.4a *3,3,6,6-Tetramethyl-9-phenyl-1,8-dioxooctahydroxanthene* (**3a**): IR (KBr, ν_{max} cm^{-1}): 3028, 2961, 1662, 1624, 1454, 1197. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.00 (s, 6H, $2CH_3$); 1.11 (s, 6H, $2CH_3$), 2.19–2.22 (m, 4H, $2CH_2$), 2.48 (s, 4H, $2CH_2$), 4.76 (s, 1H, CH), 7.22–7.13 (m, 5H, ArH).

2.4b *3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxooctahydroxanthene* (**3b**): IR (KBr, ν_{max} cm^{-1}): 3044, 2964, 1661, 1624, 1469, 1198. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.00 (s, 6H, $2CH_3$), 1.11 (s, 6H, $2CH_3$), 2.20–2.23 (m, 4H, $2CH_2$), 2.47 (s, 4H, $2CH_2$), 4.72 (s, 1H, CH), 7.20–7.27 (m, 4H, ArH).

2.4c *3,3,6,6-Tetramethyl-9-(4-Bromophenyl)-1,8-dioxooctahydroxanthene* (**3c**): IR (KBr, ν_{max} cm^{-1}): 3081, 2966, 1659, 1623, 1470, 1199. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.00 (s, 6H, $2CH_3$), 1.13 (s, 6H, $2CH_3$), 2.15–2.28 (m, 4H, $2CH_2$), 2.52 (s, 4H, $2CH_2$), 4.85 (s, 1H, CH), 7.27–8.02 (m, 4H, ArH).

2.4d *3,3,6,6-Tetramethyl-9-(3-Bromophenyl)-1,8-dioxooctahydroxanthene* (**3d**): IR (KBr, ν_{max} cm^{-1}): 3078, 2960, 1669, 1620, 1460, 1189. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.00 (s, 6H, $2CH_3$), 1.14 (s, 6H, $2CH_3$), 2.19–2.21 (m, 4H, $2CH_2$), 2.49 (s, 4H, $2CH_2$), 4.85 (s, 1H, CH), 7.28–8.09 (m, 4H, ArH).

2.4e *3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxooctahydroxanthene* (**3e**): IR (KBr, ν_{max} cm^{-1}): 3058, 2962, 1666, 1615, 1519, 1467, 1352, 1200. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 0.99 (s, 6H, $2CH_3$), 1.12 (s, 6H, $2CH_3$), 2.14–2.29 (m, 4H, $2CH_2$), 2.51 (t, j = 18.7 Hz, 4H, $2CH_2$), 4.83 (s, 1H, CH), 7.48 (d, J = 9 *Hz*, 2H, ArH), 7.62 (d, J = 8 *Hz*, 2H, ArH), 8.09 (d, J = 8 *Hz*, 2H, ArH).

2.4f *3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-1,8-dioxooctahydroxanthene* (**3f**): IR (KBr, ν_{max} cm^{-1}): 3060, 2961, 1666, 1622, 1529, 1474, 1351, 1200. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.01 (s, 6H, $2CH_3$), 1.13 (s, 6H, $2CH_3$), 2.18–2.22 (m, 4H, $2CH_2$), 2.51 (d, 4H, $2CH_2$), 4.85 (s, 1H, CH), 7.56 (t, J = 7.7 *Hz*, 1H, ArH), 7.66 (d, J = 7.6 *Hz*, 1H, ArH), 7.99 (d, j = 8.2, 1H, ArH), 8.00 (s, 1H, ArH).

2.4g *3,3,6,6-Tetramethyl-9-(4-Cyanophenyl)-1,8-dioxooctahydroxanthene* (**3g**): IR (KBr, ν_{max} cm^{-1}): 3050, 2950, 2210, 1660, 1620, 1460, 1200. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 0.99 (s, 6H, $2CH_3$), 1.13 (s, 6H, $2CH_3$), 2.17–2.23 (m, 4H, $2CH_2$), 2.5 (d, 4H, $2CH_2$), 4.78 (s, 1H, CH), 7.43 (d, J = 9.6 *Hz*, J = 1.6 *Hz*, 2H, ArH), 7.54 (d, J = 6.6 *Hz*, J = 1.6 *Hz*, 2H, ArH).

2.4h *3,3,6,6-Tetramethyl-9-(4-Hydroxyphenyl)-1,8-dioxooctahydroxanthene* (**3h**): IR (KBr, ν_{max} cm^{-1}): 3498, 3078, 2929, 1719, 1645, 1465, 1166. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.00 (s, 6H, $2CH_3$), 1.11 (s, 6H, $2CH_3$), 2.12–2.18 (m, 4H, $2CH_2$), 2.45 (s, 4H, $2CH_2$), 4.61 (s, 1H, CH), 6.77 (d, j = 8 Hz, 2H, ArH.), 6.93 (d, j= 8 Hz, 2H, ArH).

2.4i *3,3,6,6-Tetramethyl-9-(4-Methoxyphenyl)-1,8-dioxooctahydroxanthene* (**3i**): IR (KBr, ν_{max} cm^{-1}): 3050, 2958, 1658, 1625, 1439, 1261, 1195. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.00 (s, 6H, $2CH_3$), 1.11 (s, 6H, $2CH_3$), 2.20–2.22 (m, 4H, $2CH_2$), 2.47 (s, 4H, $2CH_2$), 3.74 (s, 3H, OCH_3), 4.71(s, 1H, CH), 6.76(d, J = 9 *Hz*, 2H, ArH), 7.22 (d, J = 9 *Hz*, 2H, ArH).

2.4j *3,3,6,6-Tetramethyl-9-(3-Methoxyphenyl)-1,8-dioxooctahydroxanthene* (**3j**): IR (KBr, ν_{max} cm^{-1}): 3020, 2950, 1650, 1618, 1459, 1235, 1160. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 0.99 (s, 6H, $2CH_3$), 1.12 (s, 6H, $2CH_3$), 2.30–2.45 (m, 4H, $2CH_2$), 2.54–2.71 (m, 4H, $2CH_2$), 3.81 (s, 3H, OCH_3), 4.83 (s, 1H, CH), 6.69-6.71 (dd, J = 8.0 *Hz*, J = 1.6 *Hz*, 1H), 6.89-6.95 (m, 2H), 7.17 (t, J = 8.0 *Hz*, 1H).

2.4k *3,3,6,6-Tetramethyl-9-(2-Methoxyphenyl)-1,8-dioxooctahydroxanthene* (**3k**): IR (KBr, ν_{max} cm^{-1}): 3015, 2950, 1660, 1623, 1490, 1250, 1198. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 0.97 (s, 6H, $2CH_3$), 1.11 (s, 6H, $2CH_3$), 2.14–2.23 (m, 4H, $2CH_2$), 2.39–2.48 (d, j = 17.4, 4H, $2CH_2$), 3.79 (s, 3H, OCH_3), 4.87 (s, 1H, CH), 6.77 (d, J = 8 *Hz*, 1H, ArH), 6.89 (dt, J = 7.4 *Hz*, J = 1.2 *Hz*, 1H, ArH), 7.12 (m, 1H, ArH), 7.43 (dd, J = 7.4 *Hz*, J = 1.6 *Hz* 1H,ArH).

2.4l *3,3,6,6-Tetramethyl-9-(4-Hydroxy-3-methoxyphenyl)-1,8-dioxooctahydroxanthene* (**3l**): IR (KBr, ν_{max} cm^{-1}): 3694, 3065, 2972, 1665, 1608, 1410, 1169. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 1.00 (s, 6H, $2CH_3$), 1.09 (s, 6H, $2CH_3$), 2.20 (s, 4H, $2CH_2$), 2.44 (s, 4H, $2CH_2$), 3.88 (s, 3H, OCH_3), 4.65 (s, 1H, CH), 5.46 (s, 1H), 6.53-6.58 (dd, J = 2.0, 8.1 *Hz*, 1H), 6.71 (d, J = 8.2 *Hz*, 1H), 7.00 (d, J = 2.0 *Hz*, 1H).

2.4m *14-(Phenyl)-14H-dibenzo[a,j]xanthene* (**4a**): IR (KBr, ν_{max} cm^{-1}): 3050, 1620, 1470, 1250. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 6.51 (s, 1H, CH), 6.99–8.43 (m, 17H, ArH).

2.4n *14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene* (**4b**): IR (KBr, ν_{max} cm^{-1}): 3069, 1622, 1459, 1240. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 6.49 (s, 1H, CH), 7.11–8.35 (m, 16H, ArH.)

2.4o *14-(3-chlorophenyl)-14H-dibenzo[a,j]xanthene* (**4c**): IR (KBr, ν_{max} cm^{-1}): 3073, 2900, 1619, 1456, 1239. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 6.51 (s, 1H, CH), 6.96–8.37 (m, 16H, ArH).

2.4p *14-(2-chlorophenyl)-14H-dibenzo[a,j]xanthene* (**4d**): IR (KBr, ν_{max} cm^{-1}): 3055, 2920, 1625, 1410, 1256. ^{1}H NMR (300 *MHz*, DMSO-d_6; ppm): δ 5.69 (s, 1H, CH), 5.82–7.65 (m, 16H, ArH).

2.4q *14-(4-Bromophenyl)-14H-dibenzo[a,j]xanthene* (**4e**): IR (KBr, ν_{max} cm^{-1}): 3030, 1624, 1429, 1254. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 6.63 (s, 1H, CH), 7.32–8.44 (m, 16H, ArH.).

2.4r *14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthene* (**4f**): IR (KBr, ν_{max} cm^{-1}): 3065, 1621, 1458, 1250. ^{1}HNMR (300 *MHz*, DMSO-d_6, ppm): δ 6.62 (s, 1H, CH), 7.46–8.31 (m, 16H, ArH).

2.4s *14-(3-Nitrophenyl)-14H-dibenzo[a,j]xanthene* (**4g**): IR (KBr, ν_{max} cm^{-1}): 3070, 1619, 1452, 1254. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 6.64 (s, 1H, CH), 7.29–8.44 (m, 16H, ArH).

2.4t *14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthene* (**4h**): IR (KBr, ν_{max} cm^{-1}): 3060, 1634, 1457, 1399, 1247, 1200. ^{1}H NMR (300 *MHz*, DMSO-d_6, ppm): δ 6.40 (s, 1H, CH), 7.32–8.35 (m, 16H, ArH).

2.4u *9-(4-Formylphenyl)-1,8-dioxooctahydroxanthene*: IR (KBr, ν_{max} cm^{-1}): 3021, 2968, 2845, 2756, 1661, 1620, 1454, 1197. ^{1}H NMR (300 *MHz*, $CDCl_3$, ppm): δ 0.91 (s, 6H, $2CH_3$), 1.07 (s, 6H, $2CH_3$), 2.09-2.35 (m, 8H, $4CH_2$), 5.3 (s, 1H, CH), 6.85 (d, 1H, ArH), 7.06 (d, 1H, ArH), 7.63 (d, 1H, ArH), 9.78 (d, 1H, CH), 11.68 (s, 1H). ^{13}C NMR (300 *MHz*, $CDCl_3$, ppm): δ 27.45, 27.5, 29.62, 31.44, 31.49, 32.39, 33.33, 46.41, 46.99, 115.13, 115.27, 115.55, 126.63, 126.74, 127.44, 129.79, 134.32, 135.5, 145.93, 189.34, 190.54, 191.78.

3. Results and Discussion

3.1 *Characterization of the catalyst*

The Fe nanoparticles were loaded in zeolite X and the new nanostructure zeolite (Fe-X) was characterized by FT-IR, XRD, EDS and SEM techniques.

Figure 1 shows the FT-IR spectra of Fe-X catalyst. The observed peaks at 3440 cm^{-1} and 1620 cm^{-1} are attributed to the symmetric and asymmetric stretching vibration of the OH and H-O-H groups. The absorption showed at about 1080 cm^{-1} is related to the asymmetric stretching vibration of the Si-O and Al-O bonds and the weak peak located at 470 cm^{-1} assign the bending vibrations of O-Si-O and O-Al-O.[30]

As shown in Figure 2, the XRD pattern of Fe-X catalyst (Figure 2, b) is identical to that of NaX zeolite (Figure 2, a) which proved the zeolite structure retained unchanged based on incorporation of Fe nanoparticles into the X zeolite. However, relative decreasing in the peak intensity can be related to the loading of Fe nanoparticles which its presence proved by EDS technique. Furthermore, the peak appearing at 2θ=45 clearly demonstrate the presence of Fe NPs in the zeolite X structure.[31]

Figure 3 shown the EDS spectrum of Fe-X catalyst, that confirms the presence of Fe nanoparticles in the new zeolite structure. The Si/Al ratio in the Fe-X catalyst based on EDS data is estimated about 1.07 which is in accordance with the NaX zeolite.

The morphology of Fe-X catalyst and the size distribution of the Fe NPs were determined by SEM technique (Figure 4). As clearly shown in this micrograph, nanoparticles of Fe are almost spherical and have a regular shape and the average size of nano particles was estimated about 21 nm in Fe-X nanostructure. The uniform distribution of Fe NPs on the zeolite surface is also observable.

3.2 *Catalytic activity studies*

3.2a *Synthesis of xanthene derivatives*

In continuation of our efforts on the development of new and efficient catalytic system for the green syntheses of biologically active heterocycles,[32–38] herein we wish to report a simple and highly efficient method for the preparation of two classes of xanthene derivatives by condensation of aromatic aldehyde with 2 equivalences of dimedone or β-naphtol using Fe-X as a new nanostructure catalyst.

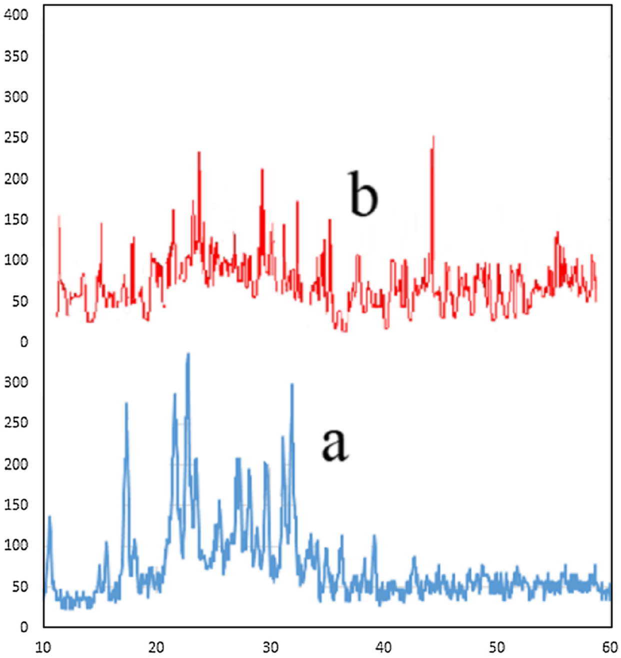


Figure 2. XRD patterns of (a) zeolite X and (b) Fe-X catalyst.

At first, to optimize the reaction condition for the synthesis 1,8-dioxooctahydroxanthens, the reaction of dimedone (2 mmol) and benzaldehyde (1 mmol) in the

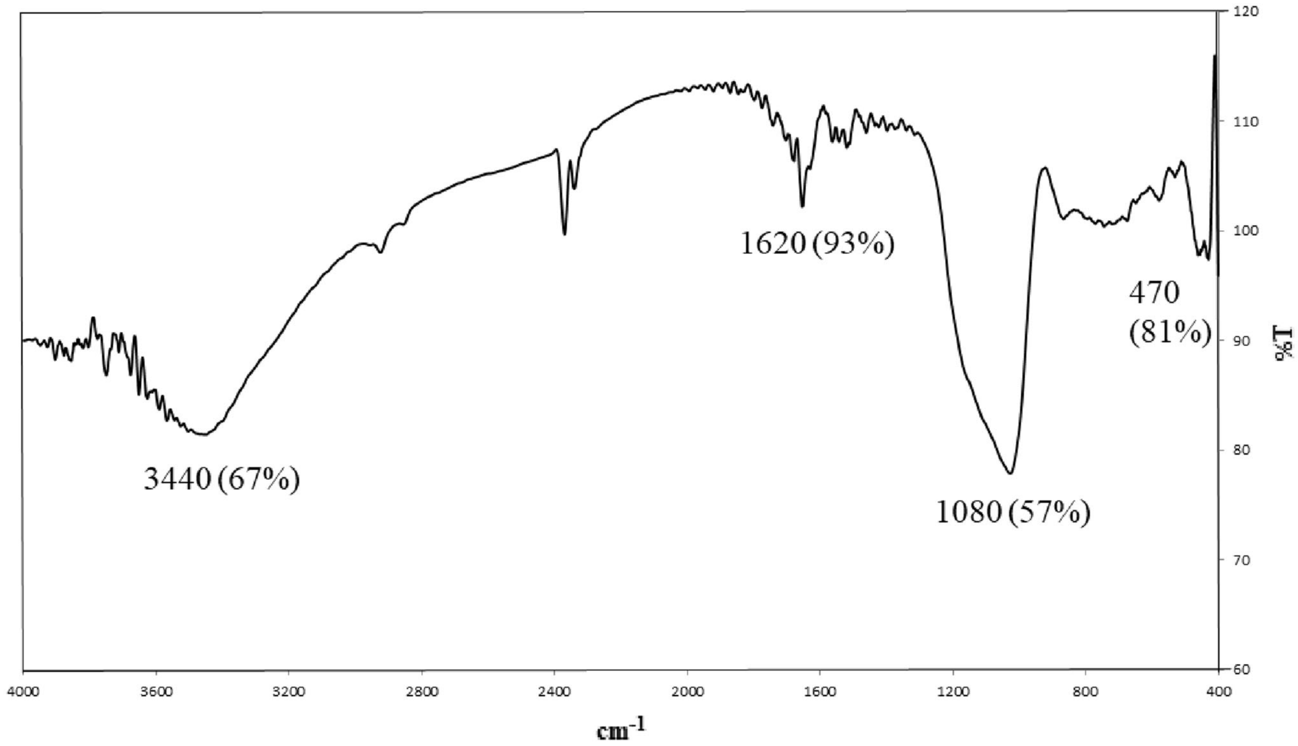


Figure 1. FT-IR spectra of Fe-X catalyst.

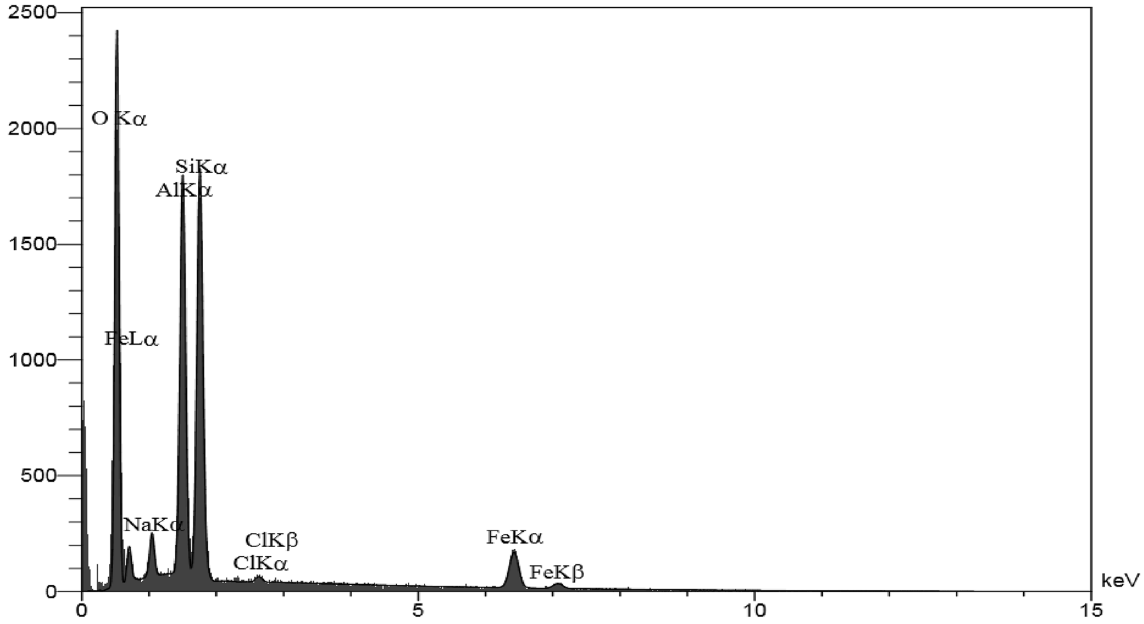


Figure 3. EDS spectra of Fe-X catalyst.

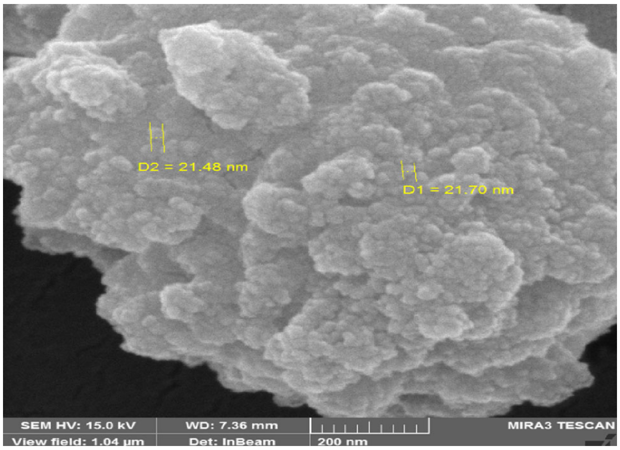


Figure 4. SEM micrograph of Fe-X zeolite.

presence of Fe-X catalyst was selected as a model reaction. The effect of solvent, amount of the catalyst and the temperature were investigated in the model reaction. As shown in Table 1, the best result was obtained in the presence of 25 mg of Fe-X at 90 °C under solvent-free condition, which led to 95% yield after 15 min (Table 1, entry 3). Also, the model reaction was performed in the presence of zeolite NaX as the catalyst and without the catalyst under optimized reaction conditions. The results show that zeolite X has low catalytic activity (Table 1, entry 13) and in the absence of catalyst, a trace amount of the product was obtained after 120 min (Table 1, entry 14).

After optimization of the reaction conditions, this procedure was extended to various aromatic aldehydes with either electron-donating or electron-withdrawing groups and dimedone under optimized reaction conditions and the corresponding 1,8-dioxooctahydroxanthenes derivative were formed in high to excellent yields and in very short times (Scheme 1, Table 2, entry 1–12).

After the successful application of Fe-X nanostructure catalyst in the synthesis of 1,8-dioxooctahydroxanthenes, we examined its applicability for preparation of 14-aryl-14H-dibenzo[*a*,*j*]xanthenes derivatives, by studying the reaction between β-naphthol (2 mmol) and different aromatic aldehydes (1 mmol) under optimized reaction condition (Scheme 2). As is shown in Table 2, the products were obtained in good yields and short times (Table 2, entry 13–20).

In Scheme 3, a reasonable mechanism has been proposed for the preparation of xanthene derivatives in the presence of Fe-X nanostructure composite.

3.3 *Chemoselectivity of the catalyst*

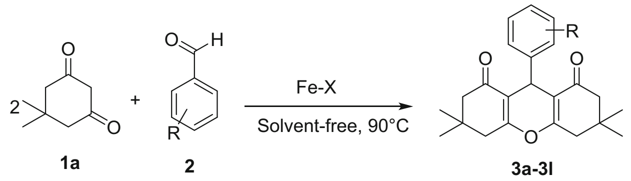
In order to investigate the selectivity of the current method terphthalaldehyde was treated with 2 and 4 equivalence dimedone under optimized conditions. It was found that in both experiments 9-(4-formylphenyl)-1,8-dioxooctahydroxanthene was exclusively generated in 90% yield after 15 min and phenylene-bis-xanthene was not observed in these reaction mixtures (Scheme 4).

Table 1. Optimization of the reaction conditions.

Entry[a]	Catalyst (mg)	Solvent	Condition	Time (min)	Yield[b] (%)
1	Fe-X (10)	–	90 °C	28	85
2	Fe-X (15)	–	90 °C	20	90
3	Fe-X (25)	–	90 °C	15	95
4	Fe-X (35)	–	90 °C	15	90
5	Fe-X (25)	–	rt	100	25
6	Fe-X (25)	–	60 °C	30	90
7	Fe-X (25)	H_2O	Reflux	50	75
8	Fe-X (25)	Ethanol	Reflux	80	55
9	Fe-X (25)	H_2O/Ethanol(1:1)	Reflux	50	60
10	Fe-X (25)	Chloroform	Reflux	40	48
11	Fe-X (25)	*n*-hexane	Reflux	40	40
12	Fe-X (25)	Ethyl acetate	Reflux	90	30
13	Zeolite X (25)	–	90 °C	15	50
14	–	–	90 °C	120	Trace

[a] Dimedone (2 mmol), benzaldehyde (1 mmol).

[b] Isolated yields.



Scheme 1. Synthesis of 1,8-dioxo-octahydroxanthens derivatives catalyzed by Fe-X.

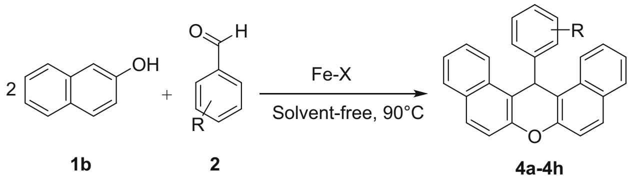
3.4 *Reusability of the catalyst*

The reusability of the catalyst was also examined in the model reaction under optimized reaction condition. After completion of the reaction, EtOH (10 mL) was added to the reaction mixture and the catalyst was separated by filtration, washed with acetone and dried at 120 °C under vacuum for 2 h. The recovered

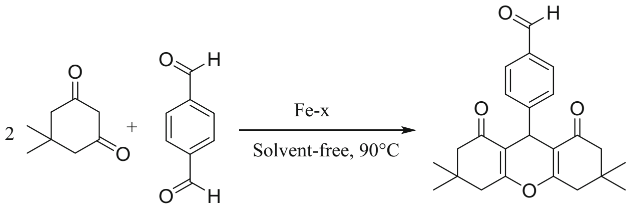
Table 2. Synthesis of xanthene derivatives catalyzed by Fe-X nanostructure composite.

Entry	1	2	Product	Time (min)	Yield (%)[a]	M.p. (°C) Found	M.p. (°C) Reported
1	1a	PhCHO	**3a**	15	95	200-203	203-205[39]
2	1a	4-Cl-C_6H_4CHO	**3b**	25	93	232-234	233-235[39]
3	1a	4-Br-C_6H_4CHO	**3c**	25	90	236-238	237-239[39]
4	1a	3-Br-C_6H_4CHO	**3d**	29	87	190-193	190-192[40]
5	1a	4-NO_2-C_6H_4CHO	**3e**	20	93	223-226	224-226[39]
6	1a	3-NO_2-C_6H_4CHO	**3f**	23	90	166-169	168-170[39]
7	1a	4-CN-C_6H_4CHO	**3g**	25	90	219-221	220-222[41]
8	1a	4-OH-C_6H_4CHO	**3h**	40	83	245-247	246-248[40]
9	1a	4-MeO-C_6H_4CHO	**3i**	60	80	243-246	243-245[41]
10	1a	3-MeO-C_6H_4CHO	**3j**	50	80	189-192	190-191[42]
11	1a	2-MeO-C_6H_4CHO	**3k**	50	80	208-210	210-212[42]
12	1a	4-OH-3-OMe-C_6H_4CHO	**3l**	40	85	225-228	225-227[40]
13	1b	PhCHO	**4a**	30	85	185-187	186-187[39]
14	1b	4-Cl-C_6H_4CHO	**4b**	40	85	289-291	290-292[39]
15	1b	3-Cl-C_6H_4CHO	**4c**	45	80	204-206	207-209[41]
16	1b	2-Cl-C_6H_4CHO	**4d**	45	80	215-217	216-218[39]
17	1b	4-Br-C_6H_4CHO	**4e**	40	85	292-294	294-295[42]
18	1b	4-NO_2-C_6H_4CHO	**4f**	40	85	310-313	312[39]
19	1b	3-NO_2-C_6H_4CHO	**4g**	45	83	214-217	212-213[39]
20	1b	4-MeO-C_6H_4CHO	**4h**	70	75	198-201	200-202[39]

[a] Isolated yields.



Scheme 2. Synthesis of 14-aryl-14H-dibenzo[*a*,*j*]xanthenes derivatives catalyzed by Fe-X.



Scheme 4. Selective synthesis of 9-(4-formylphenyl)-1,8-dioxooctahydroxanthene using Fe-X.

catalyst was reused in the same reaction. Recovery and reuse of the catalyst were repeated for 10 times, without significant decrease in this nanostructure catalyst activity. Results are summarized in Table 3.

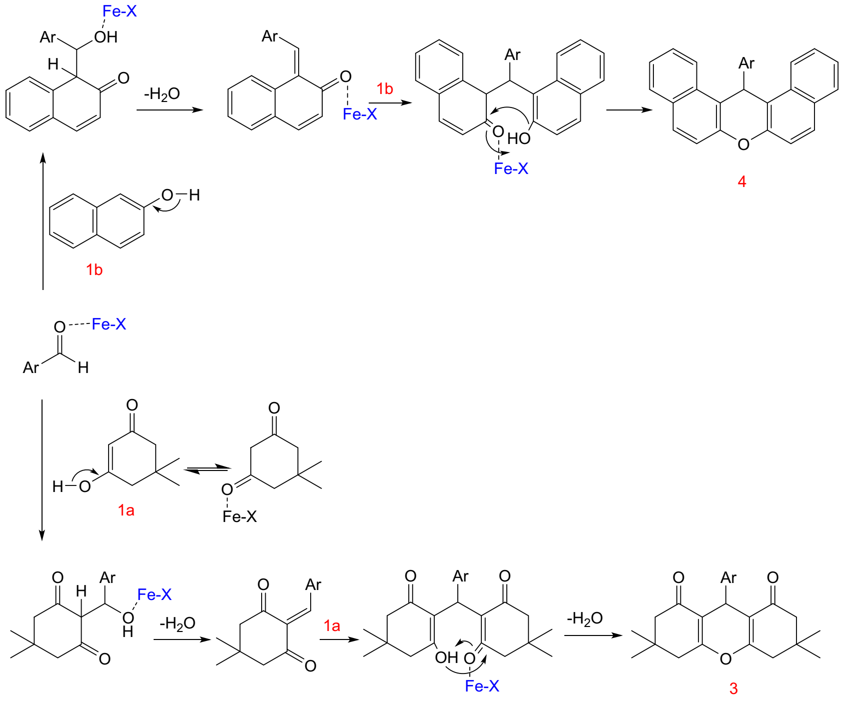
Table 3. Reusability of Fe-X in the preparation of 1,8-dioxooctahydroxanthenes from benzaldehyde and dimedone.

Run no.	1	2	3	4	5	6	7	8	9	10
Yield[a] (%)	93	93	90	90	87	85	85	85	85	85

[a]Isolated yield.

4. Conclusions

In conclusion, Fe nanoparticles loaded zeolite X (Fe-X) has been synthesized and characterized by FT-IR, XRD, EDS and SEM techniques. Spectroscopic analyses not only confirm the proposed structure of the catalyst but also, demonstrate the nano nature and crystalline character of this nanostructure zeolite. The catalytic activity of nanostructure Fe-X zeolite has been investigated in the synthesis of two series of xanthene derivatives; 1,8-dioxooctahydroxanthenes and 14-aryl-14H-dibenzo[*a*,*j*]xanthenes, from one-pot three-component condensation of aromatic aldehydes and dimedone or β-naphthol. High yields of products, short reaction time, easy work-up procedure, absence of solvent, in combination with non-toxicity, easy separation, high activity, nano character and reusability of the catalyst are a valuable advantage of this method.



Scheme 3. Proposed mechanism for the synthesis of xanthene derivatives using Fe-X.

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