Influence Parameters on Liquid Phase Reaction Preparing Terephthalic Acid from *P-* Xylene over Metal Complexes-MCM-41 Catalysts

Nho Dung Nguyen[1,*], Van Thi Tran Thi[1], Xuan Nui Pham[2], Tam Toan Tran Thanh[1]

[1]Department of Chemistry, College of Sciences, Hue University, Hue City, Vietnam
[2]Department of Oil Refining and Petrochemistry, Hanoi University of Mining and Geology, Hanoi, Vietnam

Abstract   The ordered mesoporous silica MCM-41 was anchored with metal-Shiff base complexes to produce metal-Schiff base- MCM-41 catalyst (Mn-Sal-APTES-MCM-41 and Co-Sal-APTES-MCM-41). The manganese or colbalt-Schiff base was synthesized from salicylaldehyde (Sal), (3-aminopropyl)triethoxysilane (APTES) in ethanol and manganese(II) acetate or cobalt (II) acetate. Powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), nitrogen adsorption – desorption analyses confirm the retaining of support properties after anchoring. The incorporation of Schiff base complex into the matrix causes a decreasing in the mesoscopic order, the volume of adsorbed nitrogen, the pore volume, the specific surface area, the pore diameter and a increasing in the wall thickness. The DTA-TGA and the FT-IR revealed the incorporation of the manganese or cobalt-Shiff base complex within the pores of MCM-41. On these catalysts, the liquid-phase oxidation reactions of *p*-xylene to terephthalic acid with hydrogen peroxide over obtained Shiff base complexes showed that distribution of *p*-xylene oxidation catalyzed by manganese - cobalt complexes (8:2) greatly differs from that by cobalt or manganese complex. Especially, cobalt-manganese complexes catalysts show higher activity and selectivity than neat metal acetate salts for the oxidation reaction of the methyl group under mild condition. At the reaction conditions of heterogeneous catalyst: *p*-xylene: H_2O_2: solvent molar ratio = 1:9:5 (mol/mol/mol); heterogeneous catalyst Mn-Co (8: 2); *p*-xylene: catalyst weight = 1:5 (mol/g); Me: Br molar ratio = 1: 6 (mol/mol); reaction temperature: 100 ℃; drop speed of H_2O_2 = 25 μL/min; reaction time: 72 hours.

Keywords   Manganese and cobalt Shiff base-MCM-41 catalyst, *p*-xylene liquid oxidation

1. Introduction

The selective oxidation of aromatic hydrocarbons into the corresponding oxygen-containing compounds such as alcohols, aldehydes and carboxylic acids is animportant industrialarea and also an academic interest [1]. In particular, the products of selective oxidation reaction of *p*-xylene are taken a high interest since alcohols, aldehydes for pharmaceutical industry andespecially, terephthalic acid for generous use in the polymer industry. The industrial production of alcohols, aldehydes or terephthalic acid is carried out mainly by oxidation of *p*-xylene in the presence of metal complexes as homogeneous catalysts [2-4]. These transition metal complexes are good oxidation catalysts. However, these homogeneous catalysts suffer from several problems, such as difficult separation and non-reusable ability. It would be desirable to develop more eco-friendly reusable heterogeneous catalysts for this process because most of homogeneous catalysts have environmental disadvantages. These problems can be solved by anchoring the homogeneous catalysts onto chemically modified support materials. Mesoporous silica materials have attracted attention due to their large tunable pore dimensions, high surface and diversity in surface functionalization [5]. They are also ideal supports for preparing catalysts containing anchored transition metal complexes for some different reactions [6].

Several studies have been reported as somesuch "pseudo-heterogeneous" catalystscontaining metal complexes [6-9]. However, there are few reports on anchored metal complexes onto mesoporous materials for the oxidation catalysis of aromatic hydrocarbons.

2. Experimental

2.1. Materials

All reagents: Cetyltrimethylammonium bromide (CTAB, 99%),   tetraethylorthosilicate   (TEOS),

3-aminopropyltrietylsilane (APTES), salicylic aldehyde (Sal), manganese acetate $Mn(CH_3COO)_2.4H_2O$, cobalt acetate $Co(CH_3COO)_2.4H_2O$, standards of *p*-xylene and terephthalic acid, solvents such as acetonitrile, ethyl acetate, dimethyl sulfoxide, acetic acid... were purchased from the Merck, Sigma-Aldrichor Fluka Chemical Companies. Reagents were used without extra purification, but solvents were purified by distillation. Solvents and standards (*p*-xylene and acid terephthalic) were tested by LC-MS.

2.2. Catalyst Preparation

2.2.1. Synthesis of Si-MCM-41

Si-MCM-41 was synthesized according to the method previously described by Dong Ho Park [5], Parida K.M. et al. [10]. To remove template (CTAB), 1 gram of product after drying was extracted several times with a mixture of ethanol/HCl ratio 100:1 (v: v) (100 mL ethanol and 1 mL 38% HCl) at 80 ℃ for 6 hours.

2.2.2. Synthesis of Metal-Schiff Base Complexes

The Mn-Sal-APTES and Co-Sal-APTES complexes were preparedusing procedure for metal-Schiff base complexes in literature [11, 12] with a slight modification. The received complexes were defined by their melting points, UV-Vis and IR spectroscopies.

2.2.3. Synthesis of Me-Sal-APTES-MCM-41 (Me as Co or Mn) Catalysts

Activated MCM-41 (3 g) was suspended in the absolute ethanol solution containing Schiff base complex. The mixture was stirred for 24 hrs. Ethanol was removed using a rotary evaporator and the resulting solid product dried at 80 ℃ in 24 hrs. The final product was washed with ethanol and distilled water until the washings were colourless to ensure that the non-covalently grafted complex and physisorbed metal species were removed. Further drying was carried out in an oven at 80 ℃ for 8 hrs [13].

2.3. Characterizations of Catalysts

2.3.1. Quantification of the Mount of the Metal in Catalyst Samples and Determination of Material Morphology

The catalyst sample (0.2 g) was digested by HNO_3/H_2SO_4 (3:1, v/v), then the mixture was filtered. Repeat until remaining residue was colourless. The total of the metal was determined by flame atomic absorption spectroscopy of Perkin Elmer 3110 at the wavelength of 240.7 nm.

Powder X-ray diffraction patterns were recorded on a D8-Advance Bruker with CuK_α radiation ($\lambda = 1.5406$ nm). N_2 adsorption − desorption isotherms were obtained on a Micromeritics Tristar 3000 sorptometer. Prior to analysis, the sample were outgassed at 180 ℃ in 6 hrs. BET surface areas were calculated from the linear part of the BET plot. Pore size distributions were calculated using the adsorption branches of the N_2 isotherms and the Barret-Joyner-Halenda

(BJH) method. The images of scanning electron micrograph (SEM) and transmission electron microscopy (TEM) were taken using a Hitachi S4800, operating at an accelerating voltage of 200 kV.

2.3.2. Determination of the Interaction between Grafted Complex and the Surface of Si-MCM41

Infrared data were registered on KBr pallets using a Shimadzu IR Prestige-21 spectrometer (Japan). Thermal gravimetric and differential thermal analysis (TG-DTA) were performed with a TG Setaraminstrument (France) in the air of argon (100-1000 ℃).

2.4. Catalytic Oxidation of P-Xylene in Liquid Phase

2.4.1. Catalytic Oxidation Reaction

Oxidation reaction of *p*-xylene was carried out according to the following procedure: 20 mL of *p*-xylene and precisely weighed catalyst were added into a 100 mL tree-neck flask with magnetic stirring. Hydroperoxide was introduced into the flask at a rate while the temperature was kept at a defined value. The contents of hydroperoxide were determined by iodometric method.

2.4.2. Analysis of Oxidation Products

The oxidation products of *p*-xylene were identified by GC-MS 7890A-5975C with a (30 m x 250 μm x 0.25 μm) HP-5MS column, 45-250 ℃ (45 ℃ in 2 mins, 4 ℃ /min to 200 ℃, 15 ℃ /min to 250 ℃ and kept in 5 mins) and by LC-MS co-injection of standard compound. They were quantified by LC-MS Series 2A Shimadzu (Japan) with UV 254 nm) detector and SPD-10ADVP column, eluent consisting of 1% acetic acid: acetonitrile with ratio 20: 80 to 40: 60 (w/w); with flow rate of 1 mL to 1.5 mL. min^{-1}.

3. Results and Discussion

3.1. Synthesis and Characterization of Me-Sal-APTES-MCM-41 (Me as Co or Mn) Catalysts

3.1.1. XRD of Me-Sal-APTES-MCM-41 (Me as Co or Mn) Catalysts

The small angle XRD patterns of Si-MCM-41, Co-Sal-APTES-MCM41 and Mn-Sal-APTES-MCM-41 samples containing different molar contents of metal-Schiff base complex are shown in Figure 1.

While the amount of cobalt initially introduced onto MCM-41 was 2.0; 4.0; 8.0 and 10.0 mol%, those determined by AAS was 0.70; 0.81 and 0.97 mol%, the respective ratios was 35.0, 20.3 and 12.1%. With the same amount of manganese initially introduced, the data determined by AAS was 0.73; 2.19 and 3.38 mol%, the respective ratios was 36.5, 54.8 and 42.3%, these are higher compared with Co-Sal-APTES-MCM-41. The ratio of metal complexes

grafted onto Mn-Sal-APTES-MCM-41 were higher than that in Co-Sal-APTES-MCM-41.

For the pure form of silicon (without metal complex), XRD diagrams showed three sharp diffraction peaks indexed as the (100), (110), (200) reflections of the hexagonal lattice of mesoporous MCM-41 [14]. However, the intensity of peaks became weaker for modified MCM-41 samples, indicating the introduction of metal organic complexes into the mesoporous of MCM-41. It could be seen that the intensity of the peaks for the (110) and (200) reflections clearly decreased. The reasons may be the lowering of local order, the variation in wall thickness or the result of less scattering contrast between the channel wall of the inorganic silicate framework and the organic complex of metal present in the pores. This show that the presence of metal organic complexes have self-directed disruption of the micelle structure of surfactants and silica precursors [14]. However, the position of the (100) reflection remained the same in low angles, indicating that the basic hexagonal pore framework of materials was still kept [6].
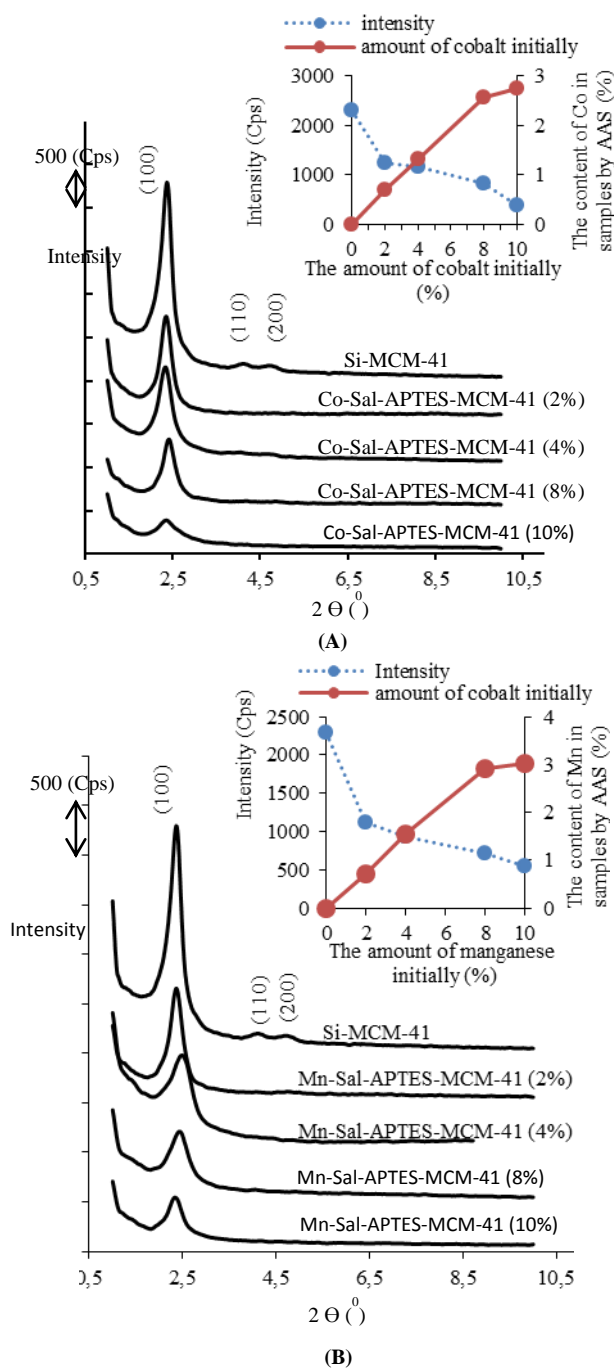

Figure 1. The X-ray diffraction patterns and the content of metal in samples (determined by AAS) of: (A) Co-Sal-APTES-MCM-41, (B) Mn-Sal-APTES-MCM-41

3.1.2. The Nitrogen Adsorption - Desorption Isotherms and Pore Size Distributions

Nitrogen adsorption-desorption diagrams are given in Figure 2 show all the samples exhibited typical IV shape isotherms of mesoporous framework. The parameters obtained from the schema nitrogen adsorption-desorption are given in Figure 2. The pore diameter of Si-MCM-41 was 23 Å, it is increased with the presence of cobalt complexes (35 Å) and manganese complexes (39.4 Å) in the pores. It is in accordance with the classification of IUPAC mesoporous materials [15], the hexagonal pores remained intact. However, the foot of the pore size distribution curves of modification materials was larger, demonstrating that the regular arrangement of the pores was lower. The pure silica material had a sharp capillary condensation steps at relative pressures of $0.2 < p/p_0 < 0.4$ and a large surface area (971.60 m^2/g). The shift to low relative pressure of $p/p_0 > 0.4$ was demonstrated the introduction of bulky metal organic complex. The other hand, the surface area of modified samples obtained from the schemes was 375.96 m^2/g and 581.60 m^2/g, it strongly decreased compared to that of Si-MCM-41. These data were consistent with the XRD results and assigned to the presence of metal organic complexes which may have been modified into the capillary of materials.
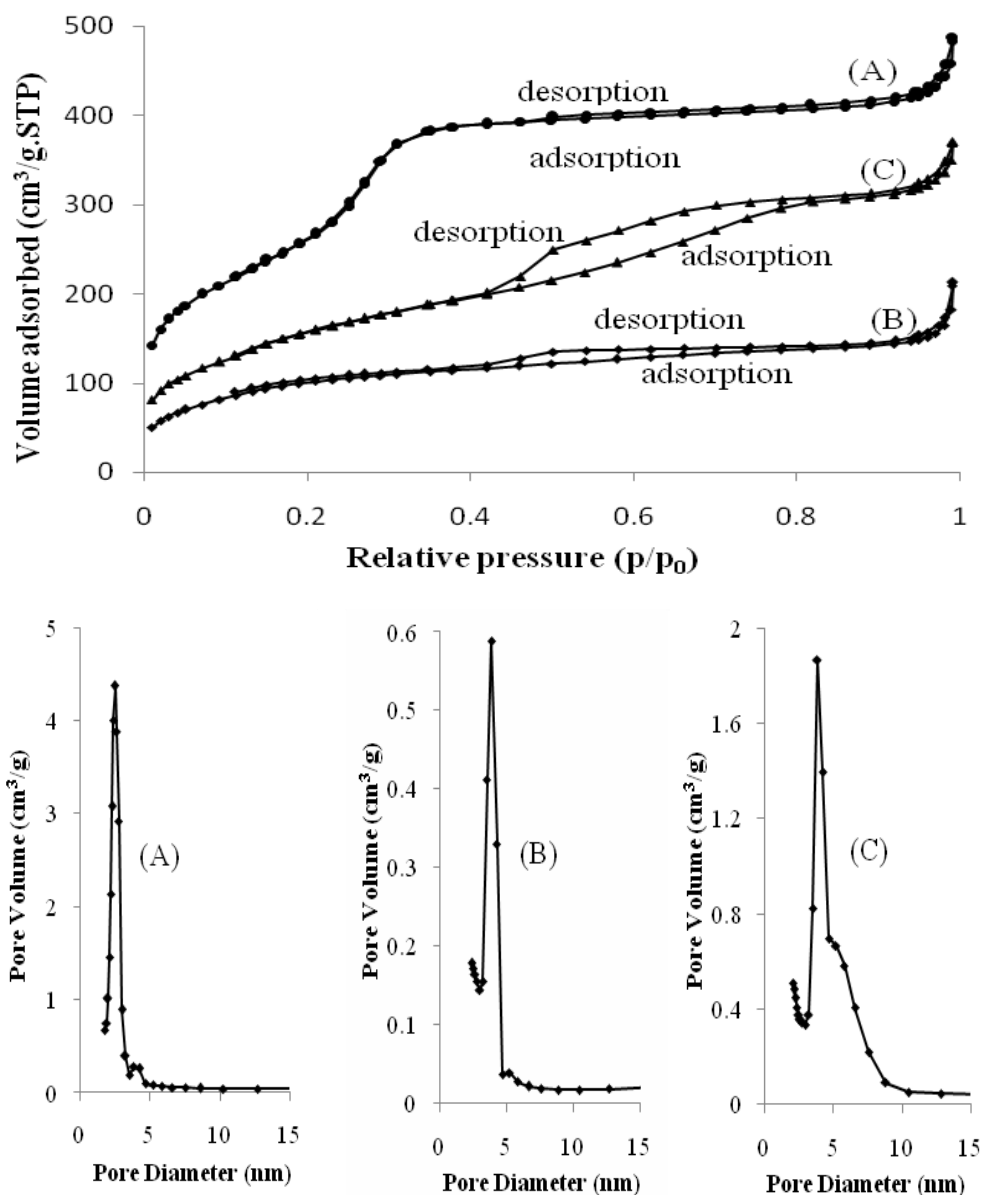

Figure 2. The nitrogen adsorption – desorption isotherms and pore size distributions of: (A) Si-MCM-41, (B) Co-Sal-APTES-MCM-41, (C) Mn-Sal-APTES-MCM-41
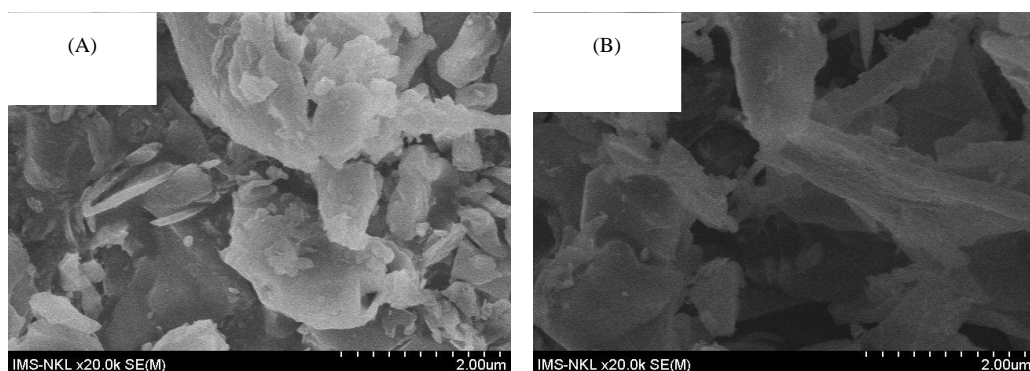
3.1.3. The SEM and TEM Images

Figure 3. The SEM images of (A): Si-MCM-41; (B): Mn-Sal-APTES-MCM-41
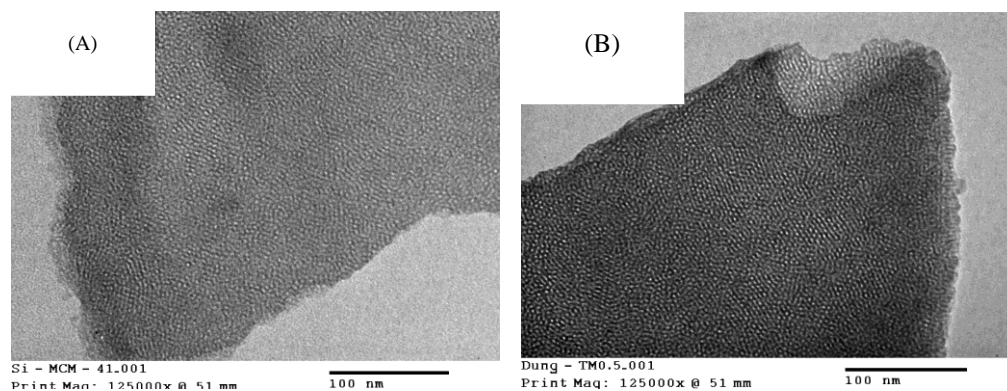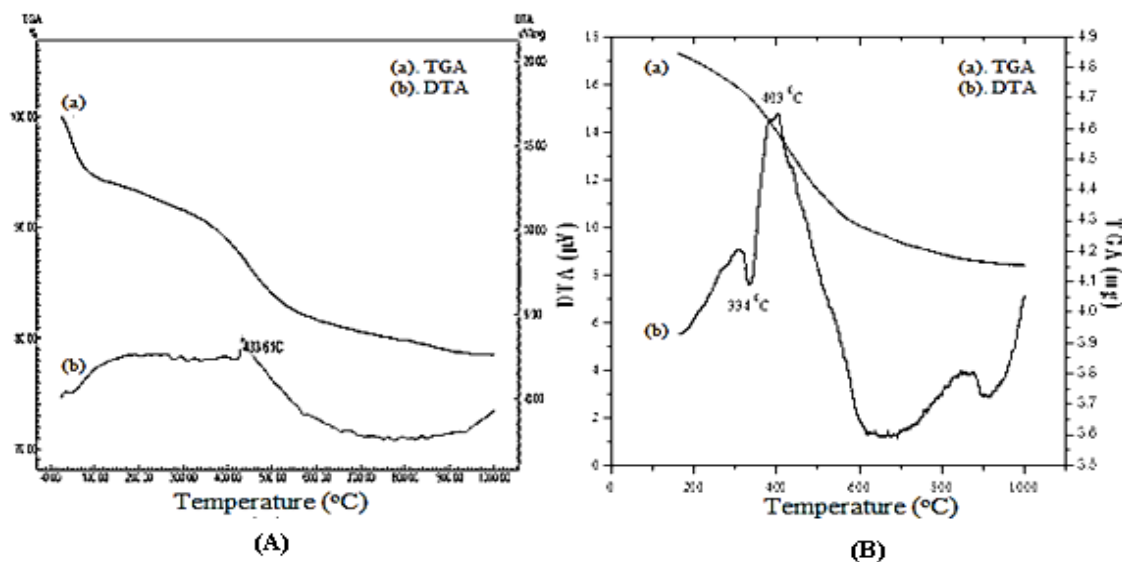

Figure 4. The TEM images of (A): Si-MCM-41; (B): Mn-Sal-APTES-MCM-41

*The initial introduced amount of metal (mol%)/ the determined amount of metal by AAS (mol%)

Figure 5. The TGA-DTA diffractions of: (A) Co-Sal-APTES-MCM-41 (0.2/0.70)*; (B) Mn-Sal-APTES-MCM-41 (0.2/0.73)*

3.1.4. The TGA-DTA Diffractions

The TGA-DTA curves of some catalysts are shown in Figure 5. Both the samples were seen a mass loss below 100 ℃ due to the remove of pthysically adsorbed water and solvent inside the pores. In the TGA-DTA of Co-Sal-APTES-MCM41, there was a large mass loss at 433.6 ℃ and in the Mn-TGA-DTA, that was at 334- 403 ℃, those due to the decomposition of the Sal-APTES ligands. These values were much higher than the boiling temperature of pure Sal and pure APTES (197 and 215 ℃ at 760 mmHg, respectively). These may be the signs indicating that there were formed co-valent chemical bonds between the metal organic complex and the silica surface of MCM-41. The total

of the mass loss of organic ligand for cobalt catalyst was 21.504%. The UV-Vis-DRS showed that there were Co(II) and Co(III) state, so that the content of cobalt in the Co-Sal-APTES-MCM-41 was about 0.126 mmol to 0.284 mmol, this value to suit the result determined by AAS was 0.176 mmol.g^{-1} (0.70 mol%). Similary, the total of the mass loss for manganese catalyst was 12.169%, so that the content of manganese in the Mn-Sal-APTES-MCM-41 was about 0.182 mmol.g^{-1}, that is equal to the result determined by AAS (0.73 mol%).

3.1.5. The FT-IR Spectra

The FT-IR spectra of Si-MCM-41 support, Me-Sal-APTES complexes and Me-Sal-APTES-MCM-41 catalysts are performed in the Figure 6. It could be seen that the bands can be attributed to the vibrations of O-H silanol groups, Si-O-Si inthe inorganic support and in the organic complex. Besides, it is constantly concerned with the weak absorption bandat 2970-2935 and 1540-1440 cm^{-1} corresponded to the stretching and bending C-H vibrations. The sharp peak at 1653-1627 cm^{-1} due to a C=N stretching vibration and the absorption peaks of the Me-O and Me-N were present in all spectra of metal complexes and catalysts. These confirmed the attachment of the metal organic complexes onto the surface of MCM-41.
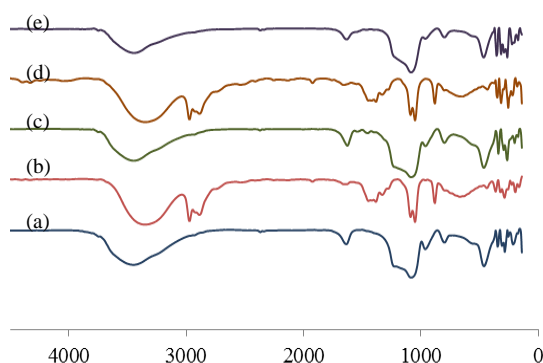

Figure 6. The FT-IR spectra of: (a)Si-MCM-41, (b) Co-Sal-APTES, (c) Co-Sal-APTES-MCM-41 catalyst, (d) Mn-Sal-APTES, (e) Mn-Sal-APTES-MCM-41 catalyst.

3.2. Oxidation Reaction of *p*-Xylene to Terephthalic acid over Me-Sal-APTES-MCM-41 Catalysts

3.2.1. Effect of Solvents

Sovent plays a important role in reaction of organic syntheisis, the solvent has to possess suitable polarity for *p*-xylene as well as other polar products transformation. Three solvents provided the convestion of *p*-xylene to 100% and terephthalic acid was also obtained. The solvent of acetic acid provided the highest selectivity to terephthalic acid (15,73%) in compared with the rest solvent (< 10%). For this reason, acetic acid solvent was chosen for next study (Figure 7).
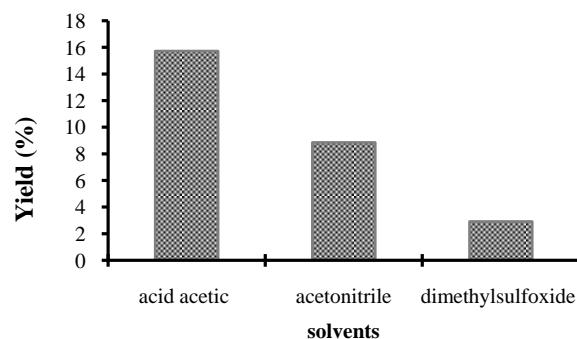

Figure 7. Effect of solvents on the production yield of terephtalic acid

3.2.2. Effect of Reaction Temperature

Table 1. *p*- xylene conversion and terephtalic acid yield at different temperatures

Solvent	Temperature (℃)	Products		
		C (%)	S (%)	Y (%)
Acetonitrile	Boiling temperature of the reaction mixture[a]	100.00	8.86	8.86
acid acetic	80	100.00	7.70	7.70
	90	100.00	15.73	15.73
	Boiling temperature of the reactionmixture[b]	100.00	38.66	38.66

C (%): Conversion of p-xylene
S (%): Selectivity to terephthalic acid
Y (%): Yield terephthalic acid
Reaction conditions of heterogeneous catalyst: p-xylene: H$_2$O$_2$: acid acetic molar ratio = 1:9:5 (mol/mol/mol); molar ratio of p-xylene: catalyst amount of Mn(1)-Sal-APTES-MCM-41 = 1:6 (mol/g); Mn:Br molar ratio   = 1: 6 (mol/mol); drop speed of H$_2$O$_2$ = 25 μL/min; reaction time:72 hrs.
(a) From 82 to 90 ℃.
(b) From 100 to 118 ℃.

In the solvent of acetic acid and acetonitril, the yield and selectivity to terephthalic acid increase as the temperature increases. The conversion of *p*-xylene is appoximately to 100% for all of temperatures studied and terephthalic acid starts to appear. The terephthalic acid yield reaches the highest value of 38.66% at boiling temperature of mixture (Table 1) (acetic acid, *p*-xylene, H$_2$O$_2$, H$_2$O).

3.2.3. Effect of the Oxidant and the Oxidant Molar Ratio

As the molar ratio of p-xylene: H$_2$O$_2$ vary from 1:6 to 1:13 the conversion reaches 100% and terephthalic acid is obtained. Table 2 shows that the terephthalic acid yield increases significantly as the amount of H$_2$O$_2$ increases and the yield increases in significantly as the amount of H$_2$O$_2$ excesses the molar ratio of 1:9. *Tert*-butylperoxide as a oxidant for ethylbenzene, cyclohexene, benzyl alcohol using nano -Co(II) was reported by [16]. In the present paper, the conversion of *p*-xylene reaches 100% in both of H$_2$O$_2$ and *tert*-buthylperoxide as oxidant but H$_2$O$_2$ provides

better selectivity to terephthalic acid. Then, H_2O_2 as oxidant with drop rate of 25 (µL/min) and molar ratio of p-xylene: H_2O_2 of 1:9 were chosen for next study.

Table 2. Reaction results with different oxidants

Oxidant	Ratio p-xylene: H_2O_2 (mol/mol)	Products		
		C (%)	S (%)	Y (%)
tert-butylperoxide	1:9	100.00	7.81	7.81
H_2O_2 30%	1: 6	100.00	17.50	17.50
	1: 7	100.00	32.11	32.11
	1: 9	100.00	38.66	38.66
	1: 11	100.00	39.32	39.32
	1: 13	100.00	38.57	38.57

Reaction conditions of heterogeneous catalyst: p-xylene: acid acetic molar ratio = 1:5 (mol/mol); molar ratio of p-xylene : catalyst amount of Mn(1)-Sal-APTES-MCM-41 = 1:6 (mol/g); Mn:Br molar ratio = 1: 6 (mol/mol); reaction temperature: 100 ^oC; reaction time:72 hrs.

3.2.4. Effect of Accelerators and Ratio of Accelerators

The molar ratio of Br:Mn = 6:1 provided the best oxidation in studied range. Then, we conducted the reaction under the condition with the molar ratio of Br:Mn = 4:1; 6:1; 8:1 (Table 3). Terephthalic acid was obtained in all cases in which the catalyst with the molar ratio of 6:1 exhibited best yield in compared that with the molar ratio of 8:1 indicating that the increase in Br leads to the reduce in yield. It could be explained that the high amount of Br supply the high amount of Br^o radicals produce, as results, the Br radicals reacted together forming Br_2.

Table 3. p- xylene conversion and terephtalic acid yield with different promoter ratios

Promoter	Ratio of accelerators: Mn (mol/mol)	Products		
		C (%)	S (%)	Y (%)
N-hydroxy-su ccinimide (NHSI)	6 :1	100.00	24.52	24.52
KBr	4 : 1	100.00	25.17	25.17
	6 : 1	100,00	**38.66**	**38.66**
	8 : 1	100,00	22.53	22.53

Reaction conditions of heterogeneous catalyst: p-xylene: H_2O_2: acid acetic molar ratio = 1:9:5 (mol/mol/mol); molar ratio of p-xylene : catalyst amount of Mn(1)-Sal-APTES-MCM-41 = 1:6 (mol/g); Mn:Br molar ratio = 1: 6 (mol/mol); drop speed of H_2O_2 = 25 µL/min; reaction temperature: 100 ^oC reaction time:72 hrs.

Falcon et al reported the p-xylene oxidation by homogeneous catalyst of $Co(OAc)_2$ và $Mn(OAc)_2$ with N-hydroxyimide as a promoter, emphasized the important role of promoter as well as $Co(OAc)_2$ và $Mn(OAc)_2$. NHSI provides the best catalytic promotion in group of N-hydoxyimide studied by [17]. NHSI also is a good catalytic promoter in the present paper but its efficiency is lower than that of KBr (Table 3).

Accoding references [18], the oxidation occur firstly in the -CH_3 group of p-xylene forming electrophile group such

as -CH_2OH, -CHO or -COOH, as resulted the oxidation of the second -CH_3 was reduced and the terephthalic acid is not obtained. In case of KBr as a promoter, Br^- anion reacts with H_2O_2 in polar solvent forming Br radical. This radical will activate the second -CH_3 forming $^•CH_2$. Upon that condition, H_2O_2 will react with $^•CH_2$ producing other radical of -$CH_2OO^•$. This radical is easily oxidized over the catalyst of Me(II) to form the second carboxyl group in terephthalic acid molecule. The KBr promoter with molar ratio of Br:Mn = 6:1 was used for further study.

3.2.5. Effect of Content of Manganese in Catalysts

The conversion of p-xylene over all catalyst samples at reaction condition is 100%. The selectivity of terephthalic acid reaches 38.66% on 2% manganese in Mn-Sal-APTES-MCM-41. The diffusion of p-xylene and products are under the strong influence of the present of Sal-APTES complex moleculars grafted on the surface and into MCM-41 mesopores, so that the content of manganese in catalyst samples is higher, the productivity of terephthalic acid is lower (Figure 8).
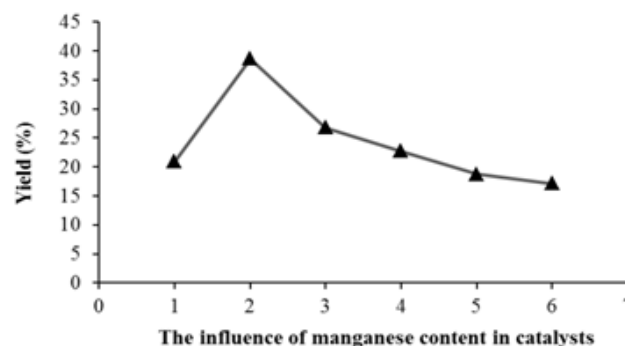

Figure 8. The influence of manganese content in catalysts on the yield of terephthalic acid

3.2.6. Effect of the Replace Manganese by Cobalt in Catalysts

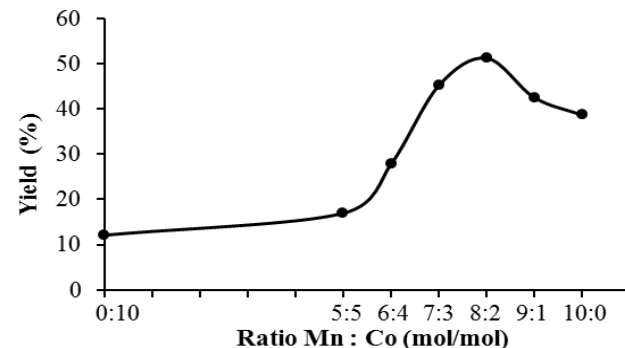The replace of manganese in catalysts by corelative cobalt, the results of reaction is showed on Figure 9.

Figure 9. Effect of ratio Mn: Co in catalysts on the yield of terephthalic acid

From Figure 9, the terephthalic acid yield increases significantly as the amount of manganese increase from 0:10 to 8:2 because catalytic activity of manganese is higher

than that of cobalt. However, the amount of manganese is 10:0 (pure manganese) the yield reduces remarkably from 51.22% to 38.66% indicating the existence of interaction between both catalytic site of cobalt and manganese as reported [19, 20]. Then, the catalyst of Mn-Co (8:2) was chosen for next study.

3.2.7. Effect of the Catalyst Weight, Solvent and Reaction Time

The effect of factors into terephthalic acid yield was estimated by optimal experiments with orthogonal of three factors with 5 points at center (Table 4). The regression equation was obtained by Minitab-15 as follows:

H = 37.206 + 8.794A − 4.801B + 7.944C − 2.349AB + 0.596AC + 1.121BC + 1.569ABC

With significant level of 0.05 p-value of coeficients is less than 0.05 indicating that all of factors contribute significantly in yield. The yield of terephthalic acid reaches 59% in experimental reaction condition.

Table 4. Effect of the catalyst weight, solvent and reaction time

Factors			Products		
p-xylene: catalyst (mol/g) (A)	*p*-xylene: solvent (mol/ mol) (B)	Reaction time (hrs) (C)	C (%)	S (%)	Y (%)
1 : 10	1 : 5	24	100.00	47.30	47.30
1 : 8	1 : 10	48	100.00	53.65	53.65
1 : 10	1 : 15	24	100.00	27.62	27.62
1 : 6	1 : 15	24	100.00	19.06	19.06
1 : 6	1 : 5	24	100.00	23.07	23.07
1 : 8	1 : 10	48	100.00	53.40	53.40
1 : 8	1 : 10	48	100.00	52.97	52.97
1 : 6	1 : 15	72	100.00	32.86	32.86
1 : 10	**1 : 5**	**72**	**100.00**	**59.00**	**59.00**
1 : 10	1 : 15	72	100.00	50.08	50.08
1 : 6	1 : 5	72	100.00	38.66	38.66
1 : 8	1 : 10	48	100.00	53.12	53.12
1 : 8	1 : 10	48	100.00	54.01	54.01

Reaction conditions of heterogeneous catalyst: p-xylene: H_2O_2 molar ratio = 1:9 (mol/mol); heterogeneous catalyst Mn-Co (8: 2); Me:Br molar ratio = 1: 6 (mol/mol); reaction temperature: 100 ^oC; drop speed of H_2O_2 = 25 μL/min.

3.3. Survey on Heterogeneity, the Possibility of Recovering and Reusing Catalysts

When using catalysts containing Schiff bases fixed on the surface of MCM-41, if the link between the Schiff base and the MCM-41 is unstable, during the oxidization reaction, catalytic centers are easily accessible to liquid phase and play as a homogenous catalyst. So, checking reliability, the possibility of recovering and reusing catalysts is an important issue in the process of studying reactions in the presence of solid catalysts.

The oxidization reaction of *p*-xylene with a catalyst

Mn-Co-Sal-APTES-MCM-41 is surveyed in the following reaction conditions:

- *p*-xylene ratio: H_2O_2: acetic acid solvent = 1: 9: 5 (mol/mol/mol)
- *P*-xylene ratio: Mn-Co catalyst molar (1) = 1: 6 (mol/g)
- Reaction temperature: 100 ℃
- Reaction time: 24 hours
- Speed of H_2O_2 into the reaction system: 25 μL/ / min

3.3.1. Survey Results on Heterogeneity of Catalyst Mn-Co-Sal-APTES-MCM-41

After some time of conducting the reaction, a mixture of reactions is centrifuged, filtered to separate the catalyst. A mixture of reactions (no catalysts) continues to be conducted, stirred and heated at 100 ℃ for 24 hours, samples are taken at various time intervals for analysis by HPLC. The results show that the level of metabolism of *p*-xylene does not change after 24 hours of reaction, so the Schiff base is not dissolved out of heterogeneous catalyst during the reaction. This is again proved by determining the content of metal in the solution after the reaction. By means of analyzing atomic absorption spectroscopy (AAS) on samples of the solution after the reaction, the results show that the content of metal in the solution after the reaction is undetected by this method (Figure 10).
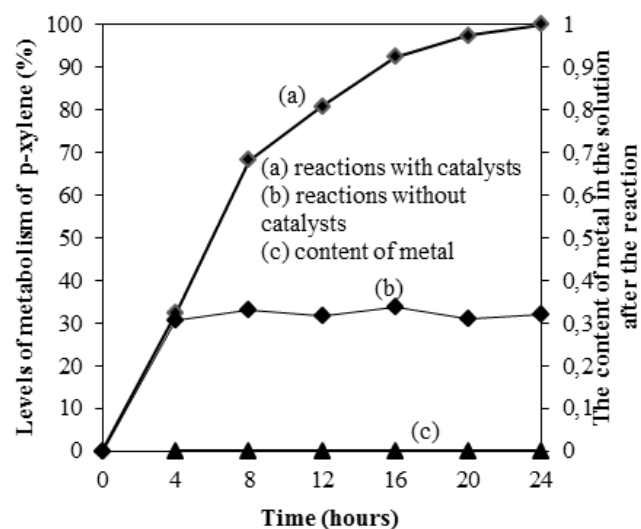

Figure 10. Checking of heterogeneous catalysiscatalyst (Mn-Co-Sal-APTES-MCM-41)

3.3.2. Survey Results on the Possibility of Recovering and Reusing Catalysts

Recovering and reusing metal catalysts are of great importance in limiting waste which seriously affects the environment and in saving costs. Besides, the recovery of catalysts limits the phenomenon of products being infected by metals. Due to the high possibility of reusing, catalysts on heterogeneous substances are always prioritized to use in processes of conducting organic synthesis reactions.

The possibility of recovering and reusing catalysts for the

oxidization of *p*-xylene is surveyed. After finishing the initial reaction, a mixture of reactions is centrifuged and catalysts are recovered for the next surveys. After the recovery, catalysts are washed many times by distilled water, acetone, n-hecxan to remove solvents and reactants, dried overnight at 100 ℃ and reused in the new reactions in the same initial conditions. In this study, the author reuses catalysts three times; in each survey, catalysts are characterized by XRD to demonstrate the structure of the material after conducting the reaction, the results are shown in Figure 11 and Figure 12.
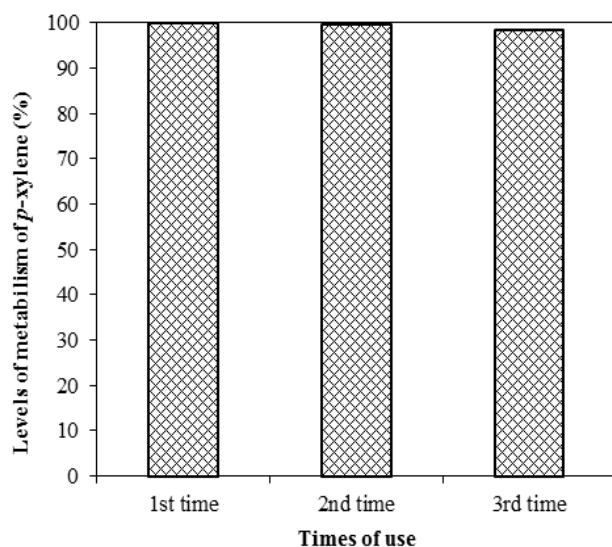

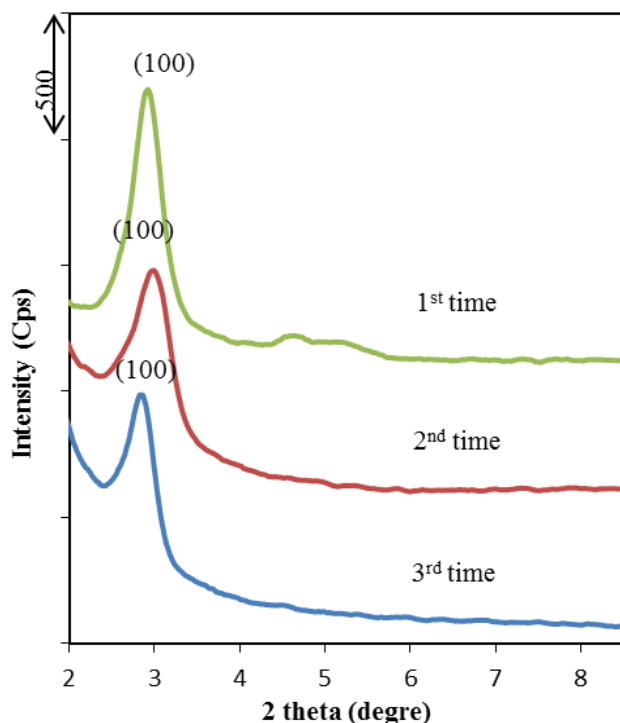**Figure 11.**   Survey on the possibility of reusing catalyst Mn-Co-Sal-APTES-MCM-41

Figure 12.   Schema of XRD after three times of reusing catalyst Mn-Co-Sal-APTES-MCM-41

3.3.3. Research Results on Comparing Performance of Creating Terephthalic Acid on Systems of Heterogeneous and Homogeneous Catalysts in the Same Reaction Conditions

To compare the effectiveness of the oxidization reaction of *p*-xylene which creates terephthalic acid on systems of heterogeneous and homogeneous catalysts in the same reaction conditions, the results are shown in Table 5.

Table 5.   Levels of metabolism and selectivity of the product in the oxidization reaction of p-xylene when using homogeneous and heterogeneous catalysts

N⁰	Catalysts	Levels of metabolism (%)	Levels of selectivity of terephthalic acid (%)
1	Mn/Co/Br	100	20.72
2	Mn-Co-Sal-APTES-MCM-41	100	59.00
3	No catalysts	20	-

Reaction conditions of heterogeneous and homogeneous catalyst: p-xylene: H_2O_2 molar ratio = 1:9 (mol/mol); heterogeneous catalyst Mn-Co (8: 2); Me:Br molar ratio = 1: 6 (mol/mol); reaction temperature: $100\,^oC$; drop speed of H_2O_2 = 25 µL/min.

Results in Table 5 show that in the same reaction conditions, when using homogeneous and heterogeneous catalysts, the level of metabolism is (100%), but the performance of creating terephthalic acid when using homogeneous catalysts (20.72%) less than heterogeneous catalysts (59.00%). This may explain that the selectivity of the product depends on the geometrical structure of catalytic materials (average capillary structure of the materials). As for the reactions without using catalysts, the metabolism level of the reaction is very poor and terephthalic acid is not produced.

4. Conclusions

The ordered mesoporous silica MCM-41 was anchored with manganese or cobalt-Schiff base complexes to produce metal- Schiff base- MCM-41 catalyst (Mn-Sal-APTES-MCM-41 and Co-Sal-APTES-MCM-41). The manganese or colbalt-Schiff base was synthesized from salicylaldehyde (Sal), (3-aminopropyl)triethoxysilane (APTES) in ethanol and mangan acetate or cobalt acetate. Powder X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), nitrogen adsorption – desorption analyses confirm the retaining of support properties after anchoring. The incorporation of Schiff base complex matrix causes a decreasing in the mesoscopic order, volume of adsorbed nitrogen, the pore volume, the specific surface area, the pore diameter and a increasing in the wall thickness. The DTA-TGA and the FT-IR revealed the incorporation of the manganese or cobalt-Schiff base complex within the pores of MCM-41.

On these catalysts, the liquid-phase oxidation reactions of

p-xylene to terephthalic acid with hydrogen peroxide over obtained Shiff base complexes showed that distribution of *p*-xylene oxidation catalyzed by manganese - cobalt complexes (8:2) greatly differs from that by cobalt or manganese complex.

Especially, cobalt-manganese complexes catalysts show higher activity and selectivity than neat metal acetate salts for the oxidation reaction of the methyl group under mild condition. At the reaction conditions of heterogeneous catalyst: *p*-xylene: H_2O_2: solvent molar ratio = 1:9:5 (mol/mol/mol); heterogeneous catalyst Mn-Co (8: 2); *p*-xylene: catalyst weight = 1:5 (mol/g); Me:Br molar ratio = 1: 6 (mol/mol); reaction temperature: 100 ℃; drop speed of H_2O_2 = 25 μL/min; reaction time: 72 hours.

ACKNOWLEDGEMENTS

REFERENCES

[1] Wei hua Yua, Chun hui Zhoub, Dong shen Tong, Tianning Xua, 2012, Aerobic oxidation of 4-tert-butyltoluene over cobalt and manganese supported hexagonal mesoporoussilicas as heterogeneous catalysts, Journal of Molecular Catalysis A: Chemical, 365, 194– 202.

[2] Chavan S.A., Halligudi S.B., Srinivas D., Ratnasamy P, 2000, Formation and role of cobalt and manganese cluster complexes in the oxidation of *p*-xylene, Journal ofMolecular Catalysis A: Chemical, 161, 49-64.

[3] Jin Won Kwak, Jae Sung Lee, Kyung Hee Lee, 2009, Co-oxidation of *p*-xylene and *p*-toluic acid to terephthalic acid in water solvent: Kinetics and additive effects Applied Catalysis A: General, 358, 54–58.

[4] Kuo-Tseng Li, Shi-Wei Li, 2008, $CoBr_2$-$MnBr_2$ containing catalysts for catalytic oxidation of *p*-xylene to terephthalic acid Applied Catalysis A. General, 340, 271-277.

[5] Dong Ho Park., 1997, Synthesis and characterization of vanadosilicatemesoporous molecular sieves MCM-41Journal of Material Chemistry, 7(1), 159-162.

[6] Yang Gang, Chen Xing, Wang Xiaoli, Xing Weihong, XuNanping, 2013, Nickel (II) complex anchored on MCM-41 for the epoxidation of styrene by oxygen Chinese Journal of Catalysis, 34, 1326–1332.

[7] Narani Anand, Kannapu Hari Prasad Reddy, Vinukonda Swapna, Kamaraju Seetha Rama Rao, David Raju Burri, 2011, Fe (III) complex anchored SBA-15 is a new heterogeneous catalyst for the cleavage of aliphatic C = C bond of styrene and its derivatives Microporous and Mesoporous Materials, 143, 132 – 140.

[8] Manirul Islama Sk., Anupam Singha Roya, Sasanka Dalapatib, Rajat Sahac, Paramita Mondala, Kajari Ghosha, Saptarshi Chatterjeed, Keka Sarkard, Nikhil Guchhaitb, Partho Mitrae, 2013, Synthesis, crystal structure and spectroscopicstudies of a cobalt(III) Schiff base complex and its use as a heterogeneous catalystfor theoxidation reaction under mild condition", Journal of Molecular Catalysis A: Chemical, 380, 94– 103.

[9] Ghasem Rezanejade Bardajee, Reihaneh Malakooti, Ibrahim Abtin, Hassan Atashin, 2013, Palladium Schiff-base complex loaded SBA-15 as a novel nanocatalyst for the synthesis of 2,3-disubstituted quinoxalines and pyridopyrazine derivatives Microporous and Mesoporous Materials, 169, 67-74.

[10] Parida K. M., Dharitri Rath, 2009, Amine functionalized MCM-41: An active and Reusable catalyst for Knoevenagel condensation reaction Journal of Molecular Catalysis A: Chemical, 310, 93–100.

[11] Fatemeh Rajabi, 2009, A heterogeneous cobalt(II) Salen complex as an efficient and reusable catalyst for acetylation of alcohols and phenols Tetrahedron Letters, 50, 395–397.

[12] Fatemeh Rajabi, Rafael Luque, James H. Clark, Babak Karimi, Duncan J. Macquarrie, 2011, A silica supported cobalt (II) Salen complex as efficient and reusable catalyst for the selective aerobic oxidation of ethyl benzene derivatives Catalysis Communications, 12, 510–513.

[13] Ghasem Rezanejade Bardajee, Reihaneh Malakooti, Fereshteh Jami, Zeinab Parsaei, Hassan Atashin, 2012, Covalent anchoring of copper-Shiff base complex into SBA-15 as a heterogeneous catalyst for the synthesis of pyridopyrazine and quinoxaline derivatives Catalysis Communications, 27, 49-53.

[14] Michael Grun, 1999, Novel pathways for the preparation of mesoporous MCM-41 materials: Control of porosity and morphology Microporous and Mesoporous materials, 27, 207-216.

[15] IUPAC, 1978, Manual of symbols and terminology Pure Apply Chemistry, 31, 578.

[16] Davood Habibi, Ali Reza Faraji, 2013, Preparation, characterization and catalytic activity of a nano-Co(II)-catalyst as a high efficient heterogeneous catalyst for the selective oxidation of ethylbenzene, cyclohexene, and benzyl alcohol, C. R. Chimie, 16, 888–896.

[17] Falcon H., Campos-Martin J.M., Al-Zahrani S.M., Fierro J.L.G., 2010, Liquid-phase oxidation of *p*-xylene using N-hydroxyimides, Catalysis Communications, 12, 5–8.

[18] Jin Won Kwak, Jae Sung Lee, Kyung Hee Lee, 2009, Co-oxidation of p-xylene and *p*-toluic acid to terephthalic acid in water solvent: Kinetics and additive effects, Applied Catalysis A: General, 358, 54–58.

[19] Hronec M., Valachová M., Masarovlc F., Cvengrosová Z., and Ilavský J. - Effect of metal catalysts on the oxidation of *p*-xylene and p-methyltoluate, Chem. Zvesti 37 (1983) 519-526.

[20] Youwei Cheng, Xi Li, Lijun Wang, Qinbo Wang, 2006, Optimum ratio of Co/Mn in the Liquid-Phase Catalytic Oxidation of *p*-xylene to Terephthalic Acid, Ind. Eng. Chem. Res, 45, 4156-4162.