

### Results and discussion

In the very first part of introduction of this thesis, few research problems and their solutions were discussed with current status of research. In addition to the status of current research about the environmental problems, catalyst materials were visualised in such a way that they can help in minimizing these problems for example low energy and heat consumption, waste product remedies, minimum release of environmental hazards and low cost of scientific procedures. Several catalyst materials are available and are playing the most important role for solution of mentioned issues. Zeolites are the best known catalyst materials with several inherent properties which have been utilised from about 200 years ago. However surprising fact beyond this speculation is that these materials are natural catalyst and have been used by nature to solve few of the mentioned issues and maintain the energy cycle of ecosystem as natural mica minerals. Zeolite and clay minerals are found to be natural purifier of water in coastal area with a limitless amount. These materials also play an important role in the degradation and catalytic reactions of nature.

In the current study, role of synthesized metal analogues of these natural catalysts was extended to check their comparative efficiency in a research oriented way. In this study, beyond the natural zeolite material, three man made or synthesized materials framework-types namely silicoaluminophosphate (SAPO-5 and SAPO-34) and aluminophosphate (AIPO-5), have been used. These synthesized and modified materials were tested for their use as a catalyst material. Then environmentally important reactions were selected. The study was carried out in a controlled way with variation in the following parametrs:

- ❖ Effect of catalysts
- ❖ Reaction time
- ❖ Catalyst loading
- ❖ Reaction temperature
- ❖ Solvents
- ❖ Catalyst recycling

These materials have a great diversity in their characteristics as catalysts and great combination of different physicochemical characteristics because of their

composition, framework structure, their building scheme, pore shape and size by which they make different combinations to obtain different catalyst materials with different properties. However in this study, the above mentioned synthesis variables were studied with main focus on following properties of catalyst materials:

1. Surface area
2. Pore size and shape
3. Strength of catalytic sites
4. Behavior of various inserted metals

#### 4.1 Catalyst efficiency and study of synthesis variables

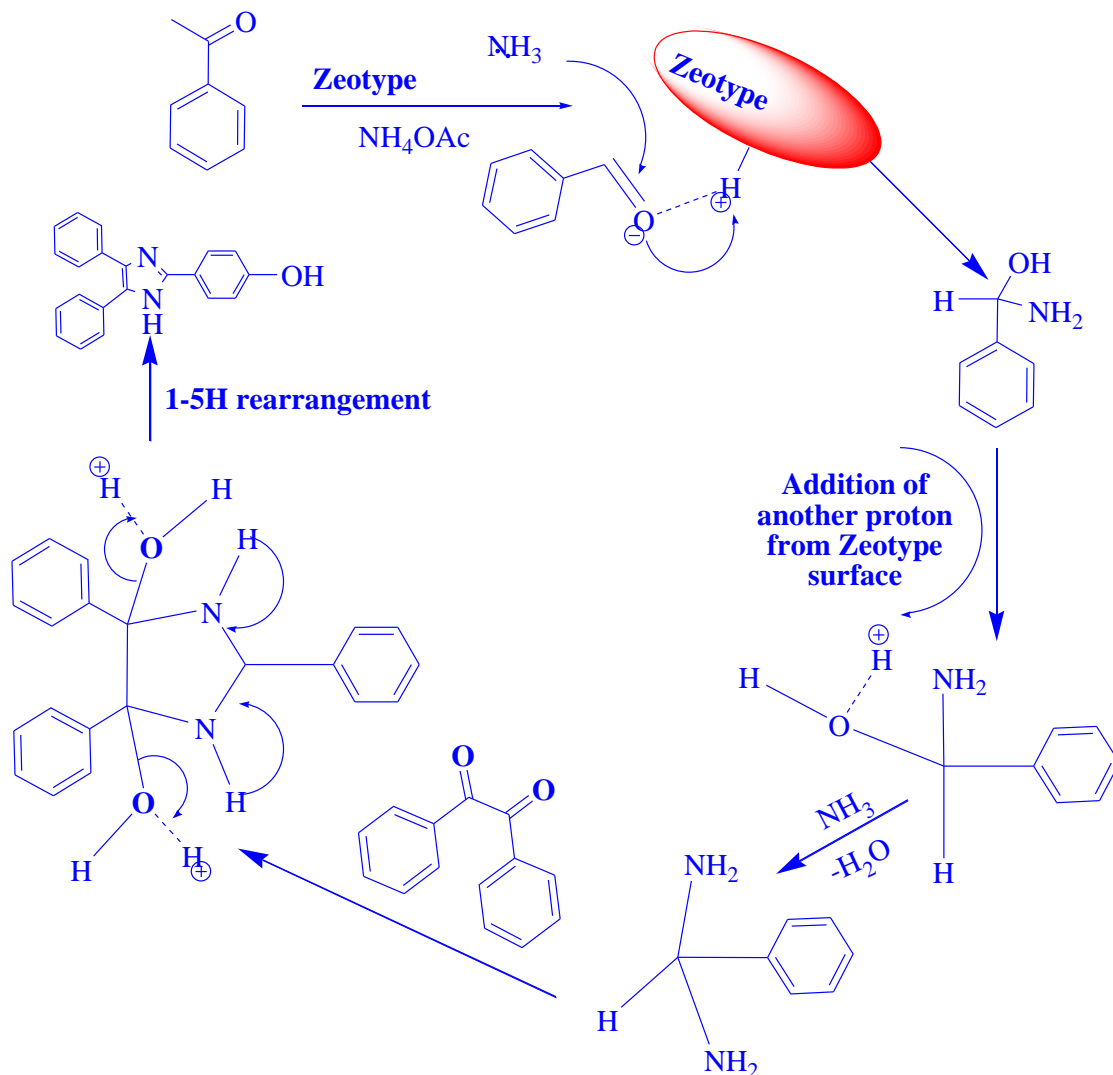
All the various forms of catalyst materials were checked for their catalytic efficiency in various reactions under controlled conditions. Synthesis of different compounds over different catalysts and their effect is observed as follow.

##### 4.1.1 Synthesis of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol (Imidazole)

The reaction was carried out according to procedure given in the scheme 2.5.1 explained in the Materials and Methods (Chapter-2). This scheme of reaction was then optimised and synthesis variables were varied over reasonable range of these variables one by one keeping the other synthesis variables constant for studying their effect on the product yield and catalytic efficiency. To avoid any artefact, reaction was performed in neat and clean glassware with Benzil, p-hydroxybenzaldehyde, ammonium acetate and catalyst. Obtained results of product were initially examined by TLC. However this reaction itself shows completion, as on the end point, reaction mixture gets solidified which can be taken as the completion point of this reaction. Reaction product was finally dissolved in ethanol and product was re-crystallized by ethanol and the product yield was measured according to given formula in previous chapter after purification of product by column chromatography.

$$\text{Product yield (\%)} = \frac{\text{Actual yield (g)}}{\text{Theoretical yield (g)}} \times 100\%$$

Proposed mechanism of synthesis is as follows.



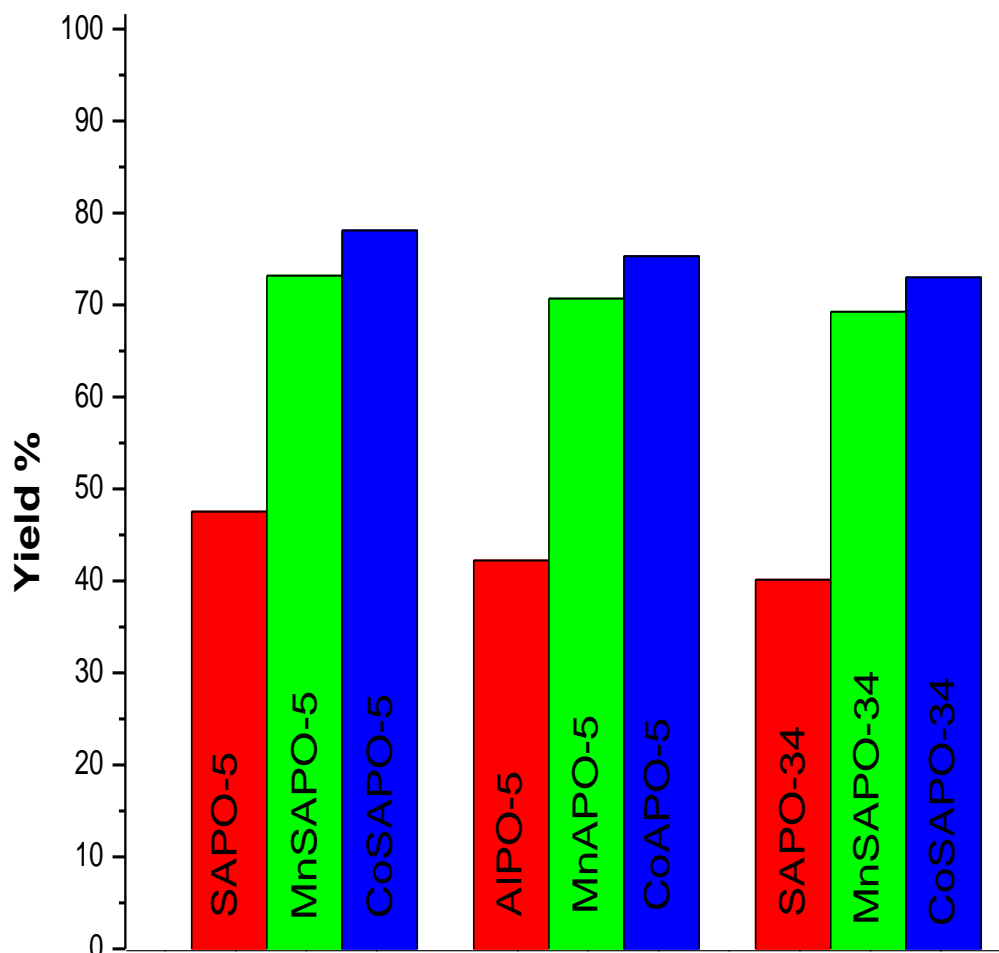
(Mechanism of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol synthesis)

#### 4.1.1.1 Efficiency of different catalysts on the yield of Imidazole

All catalyst materials with their metal analogues, were tested in this reaction of benzil, aldehyde and ammonium acetate. The reaction conditions were followed according to the scheme 2.5.1. Effect of different synthesis variables is given in the following table 4.1.1.1(a) and graph 4.1.1.1(a).

Table 4.1.1.1(a). Effect of different catalysts on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol

Catalyst form	% yield of catalytic forms		
	SAPO-5	AIPO-5	SAPO-34
Non Substituted	47.53	42.23	40.14
Mn <sup>2+</sup> Substituted	73.2	70.69	69.27
Co <sup>2+</sup> Substituted	78.1	75.3	72.99



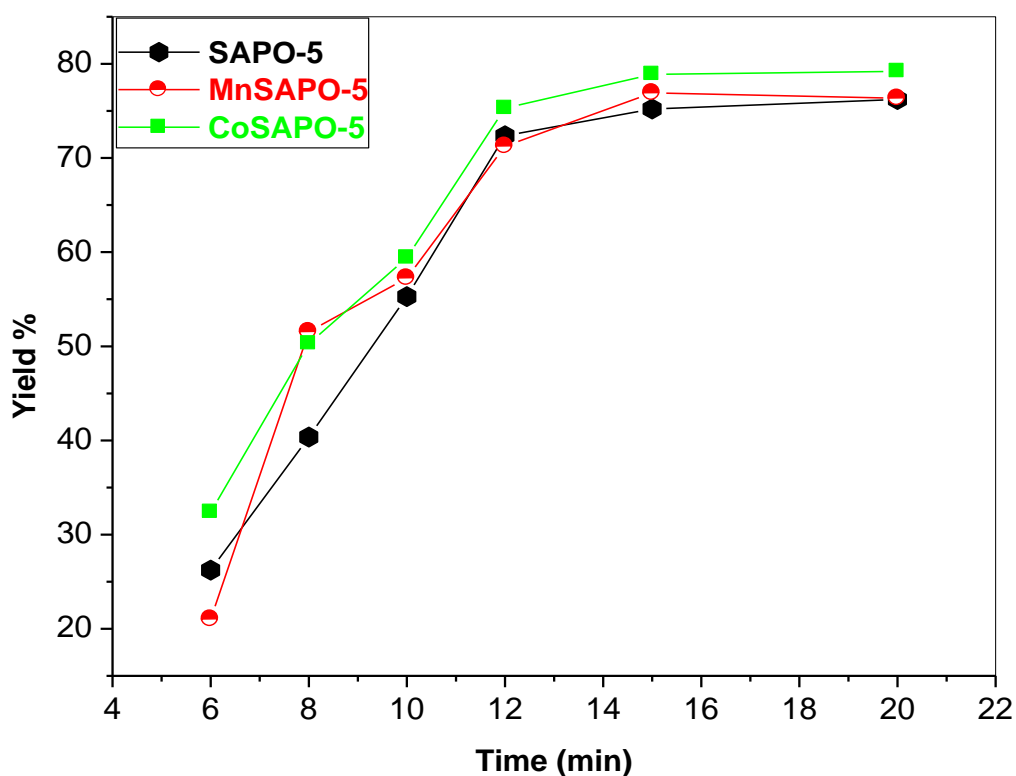
Graph 4.1.1.1(a). Effect of catalysts on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol

#### 4.1.1.2 Effect of reaction time

Reaction time has a great importance from green chemistry point of view and energy consumption. Effect of reaction time on the synthesis of Imidazole over various catalytic forms of zeotypes was observed with the same reactants following the Scheme 2.5.1 and presented in the tables 4.1.1.2(a-c) and graphs 4.1.1.2(a-c). TLC plate was developed using n-hexane and ethyl acetate as developing solvent in 7:5 ratio. Reaction aliquots were taken at different successive intervals of time and analysed using TLC plate. Reaction was continued till the appearance of single point in the TLC plate. Most suitable time was 15 minutes, however after a limit of time reaction gets solidified thus it is assumed that the reaction is not proceeding forward now. After this time, no further increase in the yield is observed because reaction gets almost completed within this period. This reaction is a condensation reaction thus the time of reaction is short because in presence of strong solid acid sites, reactants get condensed soon.

Table 4.1.1.2(a). Effect of reaction time on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

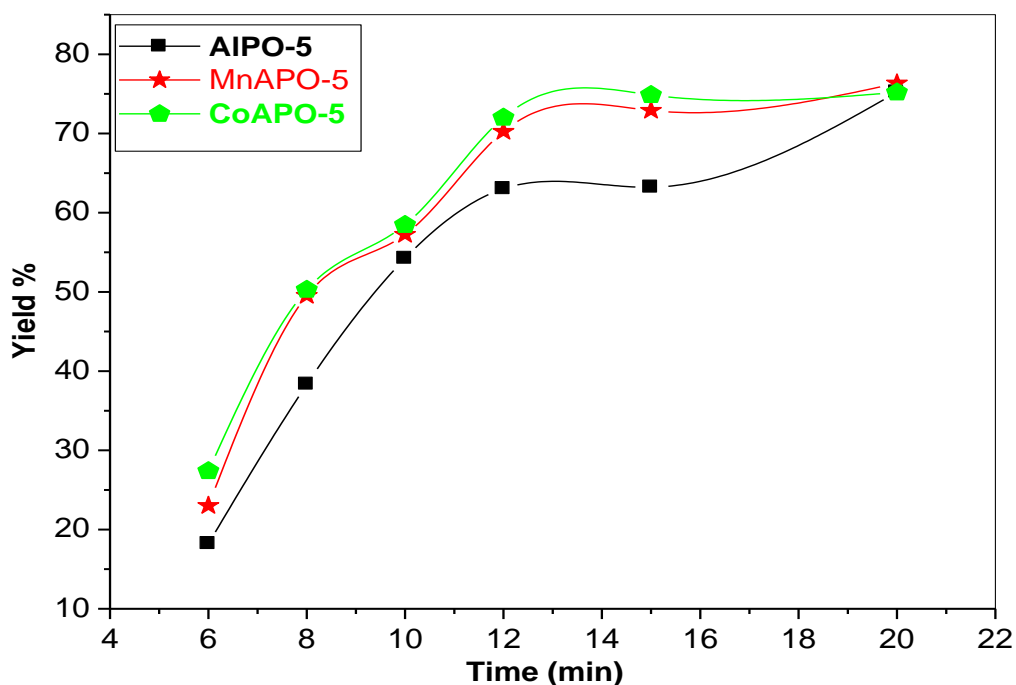
Time (min)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
6	26.22	21.02	32.4
8	40.36	51.54	50.28
10	55.28	57.25	59.41
12	72.36	71.25	75.29
15	75.21	76.91	78.88
20	76.22	76.35	79.2



Graph 4.1.1.2(a). Effect of reaction time on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

Table 4.1.1.2(b). Effect of reaction time on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various metal substituted forms of AlPO-5

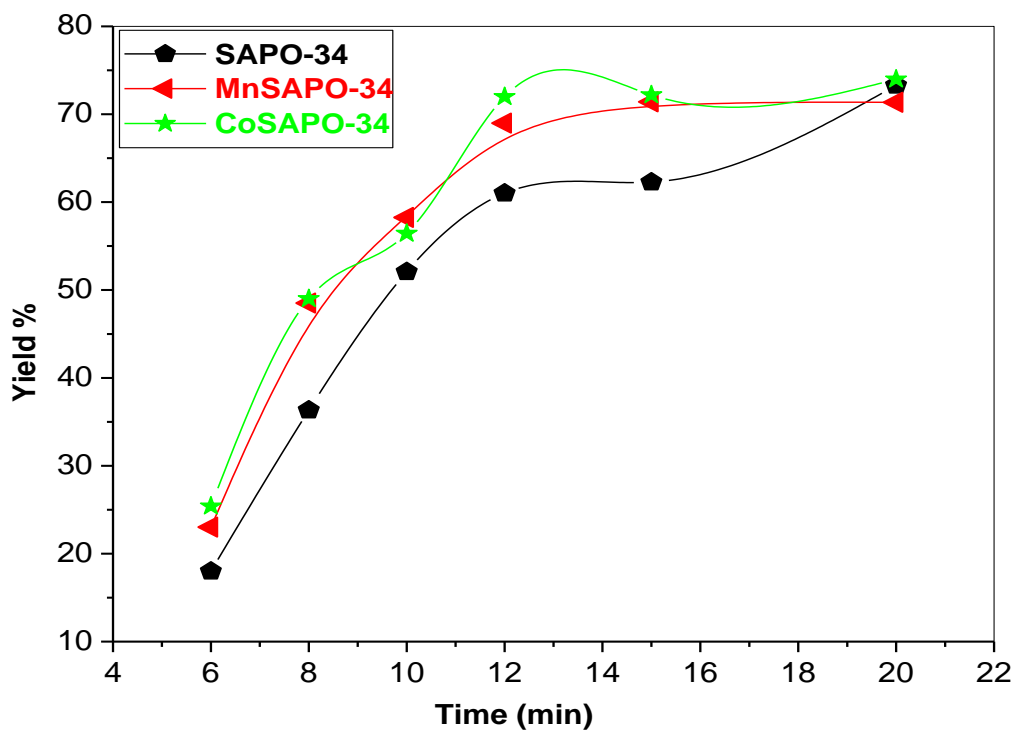
Time (min)	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
6	18.22	23.02	27.40
8	38.34	49.54	50.28
10	54.24	57.25	58.47
12	63.02	70.25	72.02
15	63.21	72.91	74.88
20	75.22	76.35	75.27



Graph 4.1.1.2(b). Effect of reaction time on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various metal substituted forms of AlPO-5

Table 4.1.1.2(c). Effect of reaction time on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various metal substituted forms of AIPO-34

Time (min)	% yield of catalytic forms		
	SAPO-34	MnAPO-34	CoAPO-34
6	18.01	23.02	25.40
8	36.34	48.51	49.00
10	52.08	58.25	56.44
12	61.02	68.99	71.99
15	62.28	71.41	72.20
20	73.29	71.35	73.99



Graph 4.1.1.2(c). Effect of reaction time on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various metal substituted forms of AIPO-34

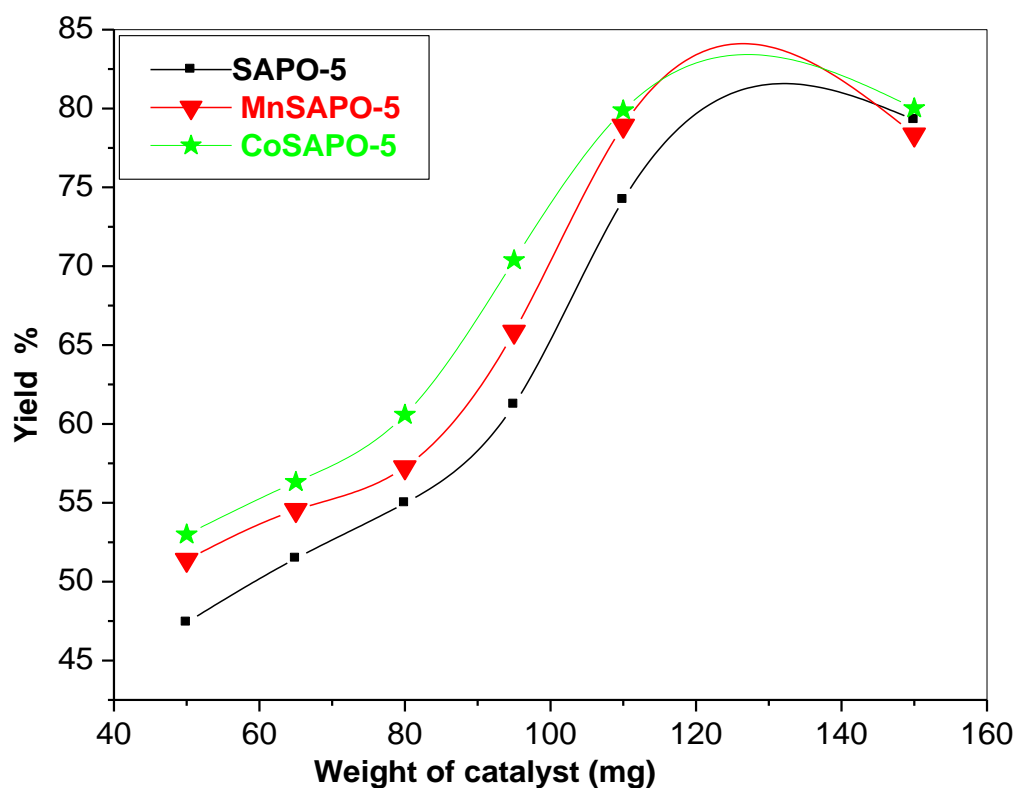


#### 4.1.1.3 Effect of weight of the catalyst

Amount of catalyst speeds up the reaction and completes reaction in a shorter time. The results obtained for this variable are straight and yield of the product is proportional to weight of catalyst employed in the corresponding reactions which are presented in tables 4.1.1.3(a-c) and graphs 4.1.1.3(a-c). The catalyst weight was varied over a reasonable range of weight that is 50-150 mg. Reaction was carried out according to the scheme 2.5.1. As the reaction was performed in a small aliquot of reactants, thus this range of weight of catalyst was reasonable. In the reaction which is performed according to the scheme 2.5.1, solvent was not taken, much amount of catalyst causes solidification of reaction mixture and reactants do not get mixed properly. Due to this fact, the amount of catalyst was taken in this range of weight. It is observed that as the amount of catalyst increases, the yield of product also increases but after 100 mg amount of catalyst reaction rate was not increasing in proportional way and also caused impurities due to un-reacted reactants (observed in TLC plate).

Table 4.1.1.3(a). Effect of weight of catalyst on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

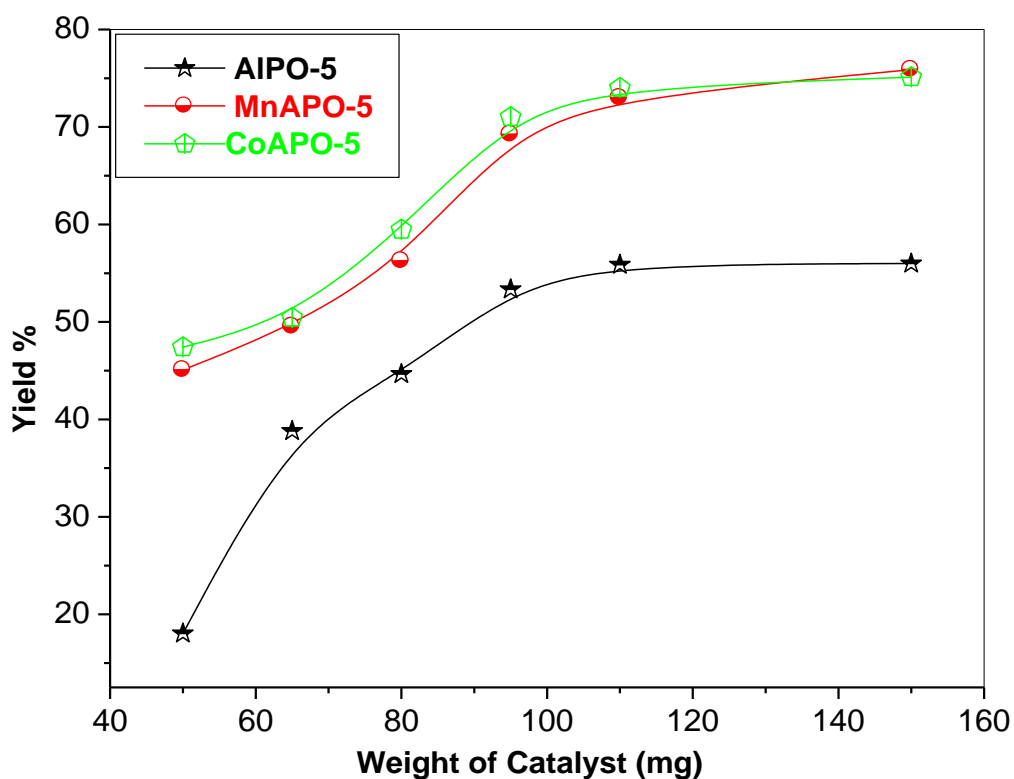
Weight (mg)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
50	47.41	51.38	52.99
65	51.47	54.54	56.32
80	54.98	57.25	60.58
95	61.22	65.85	70.38
110	74.21	78.91	79.88
150	79.28	78.35	80.01



Graph 4.1.1.3(a). Effect of weight of the catalyst on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

Table 4.1.1.3(b). Effect of weight of catalyst on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AlPO-5

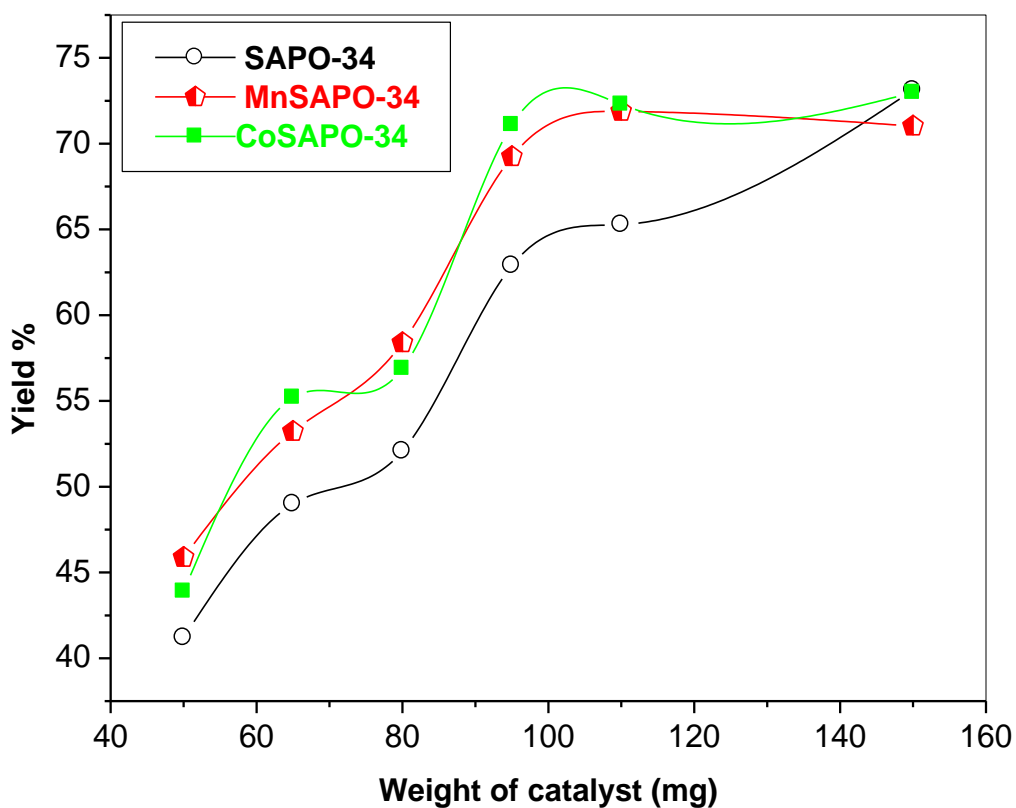
Weight (mg)	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
50	18.03	45.08	47.41
65	38.81	49.54	50.43
80	44.65	56.26	59.47
95	53.34	69.25	71.02
110	55.87	72.99	74.01
150	55.99	75.89	75.12



Graph 4.1.1.3(b). Effect of weight of the catalyst on yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AlPO-5

**4.1.1.3(c). Effect of weight of the catalyst on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34**

Weight (mg)	% yield of catalytic forms		
	SAPO-34	MnAPO-34	CoAPO-34
50	41.20	45.88	43.89
65	49.00	53.22	55.20
80	52.08	58.39	56.88
95	62.89	69.24	71.09
110	65.28	71.88	72.28
150	73.12	71.02	72.98

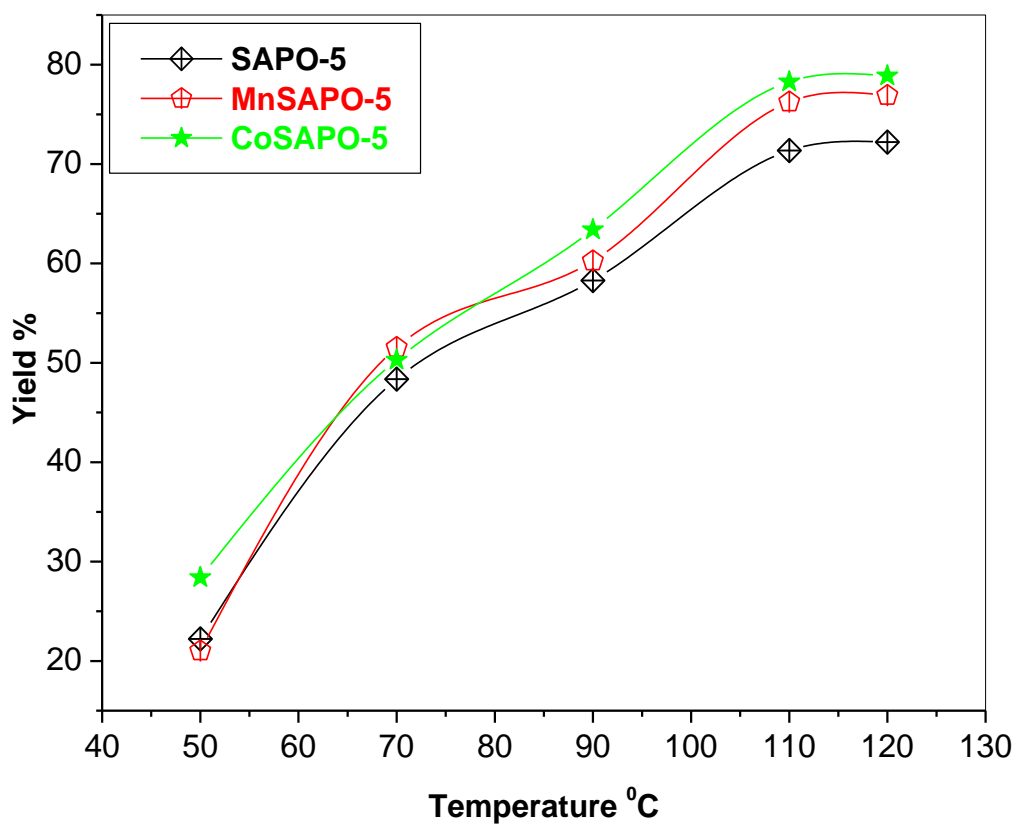
**4.1.1.3(c). Effect of weight of yhe catalyst on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34**

#### 4.1.1.4 Effect of reaction temperature

Effect of reaction temperature was studied over a range of temperature (50-120°C) for synthesis of Imidazole following the same reaction conditions explained in the scheme 2.5.1. All other synthesis variables were kept constant and temperature was varied for different reaction batches. It was found that reaction temperature has impact on the yield of product. However, reaction also proceeds at relatively low temperature efficiently because after a certain range of temperature, reactants get condensed followed by appearance of solid product material. Thus it can be concluded that in this type of reaction, after a limit of temperature range, reaction is not influenced by the temperature considerable. Probably, it may be due to very short reaction time of this reaction. Thus till the reaction temperature reaches up to more than about 100°C, reactants have been condensed to form the product and after this point no further changes are made by temperature in the yield of product. In addition to this, another fact in the support of the above consideration is that other variables like time of reaction etc., have a non straight relation to the yield of product. Thus the reaction proceeds suddenly which is clear from the tables 4.1.1.4(a-c) and graphs 4.1.14(a-c).

Table 4.1.1.4(a). Effect of reaction temperature on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenole over various catalytic forms of SAPO-5

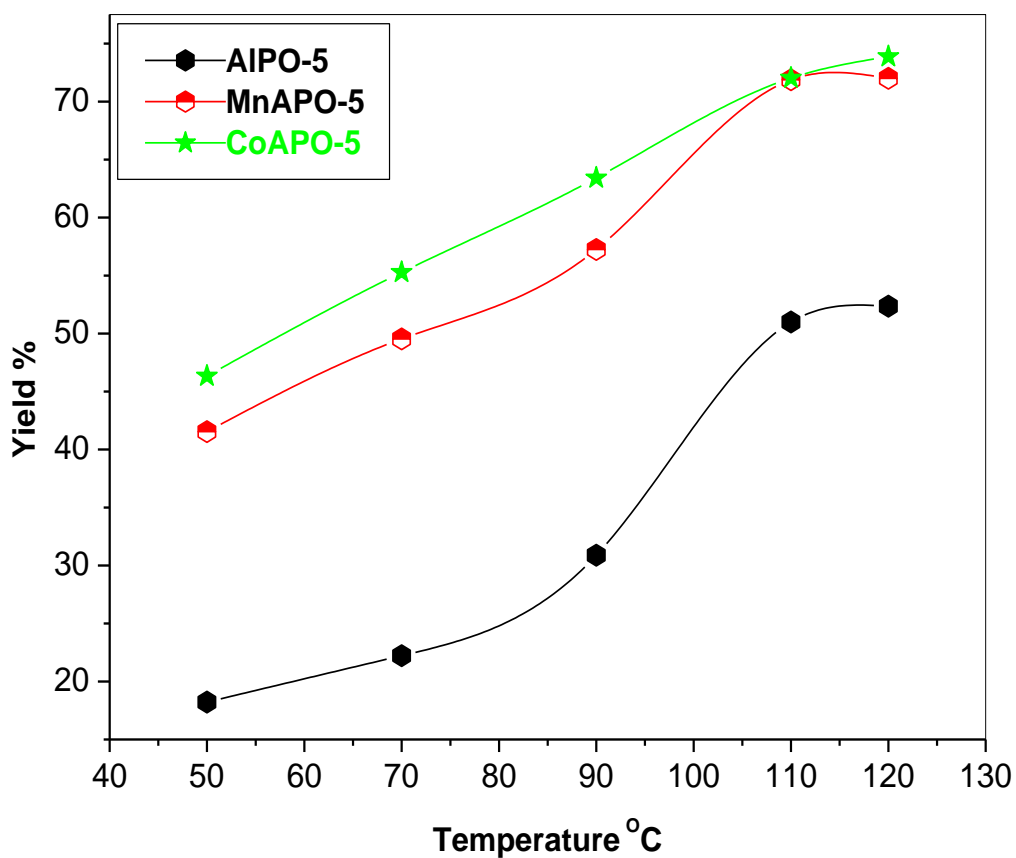
Temperature (°C)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
50	22.22	21.02	28.40
70	48.36	51.54	50.28
90	58.28	60.25	63.41
110	71.36	76.25	78.29
120	72.21	76.91	78.88



Graph 4.1.1.4(a). Effect of reaction temperature on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

Table 4.1.1.4(b). Effect of reaction temperature on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AlPO-5

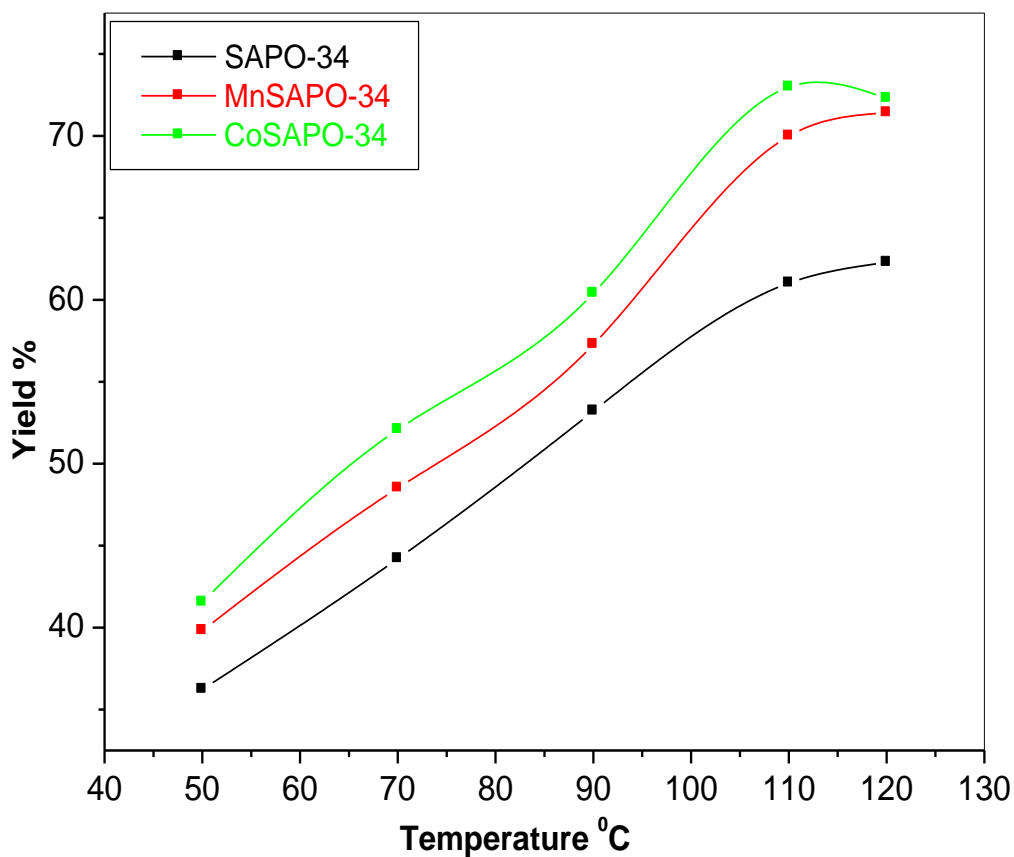
Temperature (°C)	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
50	18.22	41.54	46.33
70	22.23	49.54	55.28
90	30.89	57.25	63.41
110	50.99	71.88	72.02
120	52.36	72.00	73.88



Graph 4.1.1.4(b). Effect of reaction temperature on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AlPO-5

Table 4.1.1.4(c). Effect of reaction temperature on the yield of 4(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34

Temperature (°C)	% yield of catalytic forms		
	SAPO-34	MnAPO-34	CoAPO-34
50	36.22	39.81	41.55
70	44.25	48.51	52.08
90	53.21	57.27	60.44
110	61.02	69.99	72.99
120	62.28	71.41	72.29



Graph 4.1.1.4(c). Effect of reaction temperature on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34

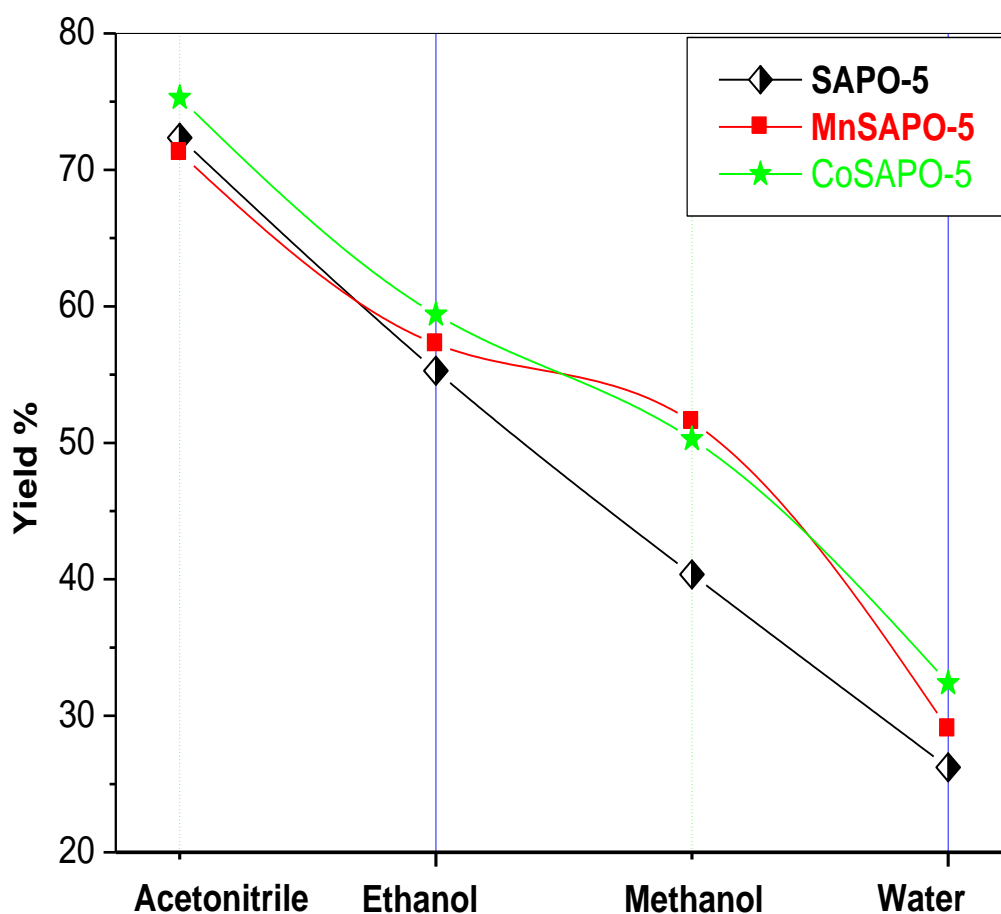


#### 4.1.1.5 Effect of solvent

Effect of the different solvents on synthesis of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of aluminophosphates and silicoaluminophosphate was studied. Reaction for the synthesis of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol was performed following the scheme 2.5.1 without use of solvent and the results obtained for product yield were excellent. To examine the effect of various solvents, reaction was performed in different solvent systems (water, ethanol methanol and acetonitrile) following the same synthesis parameters employed in scheme 2.5.1 by keeping all other parameters constant. It was observed that different solvents suppress the reaction yield in comparison to non solvent system or reaction without any solvent. The results are given in tables 4.1.1.5(a-c) and graphs 4.1.1.5(a-c). It is formulated that these solvents are polar solvents and may be adsorbed on the surface of polar zeotypes as these catalysts are having hydroxyl (free) groups on their surface. Hydrogen bonding and chemisorption of these polar solvents on the surface of catalysts may create a competition for the reactant molecules which are of organic origin and bigger in size. Thus there is a possibility of adsorption of solvent first on the surface of catalysts than the reactant molecules. Thus the equilibrium may shift towards solvent followed by a decrease in obtained surface area for the reactants. This is also confirmed by the yield of product for different solvents as the yield (acetonitrile > ethanol > methanol > water) is in order of polarity (acetonitrile 0.46 < ethanol 0.65 < methanol 0.762).

Table 4.1.1.5(a) Effect of different solvents on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

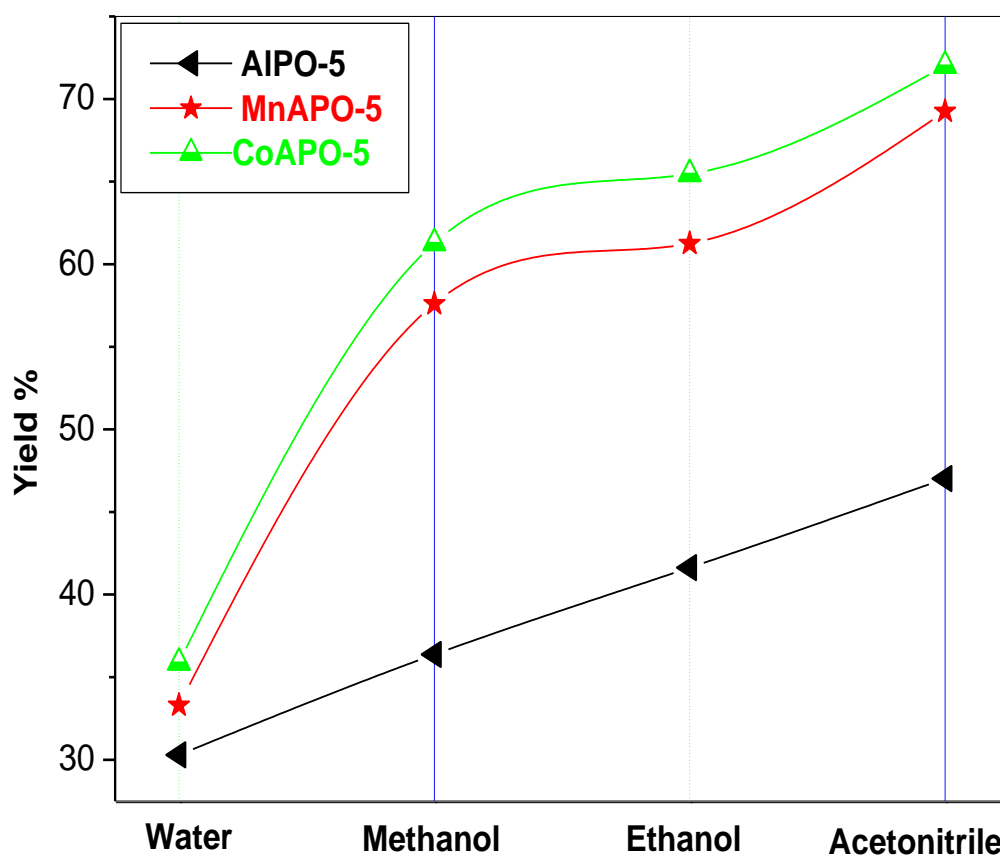
Solvent	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
Acetonitrile	72.36	71.25	75.29
Ethanol	55.28	57.25	59.41
Methanol	40.36	51.54	50.28
Water	26.22	29.02	32.44



Graph 4.1.1.5(a) Effect of different solvents on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

Table 4.1.1.5(b). Effect of different solvents on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AlPO-5

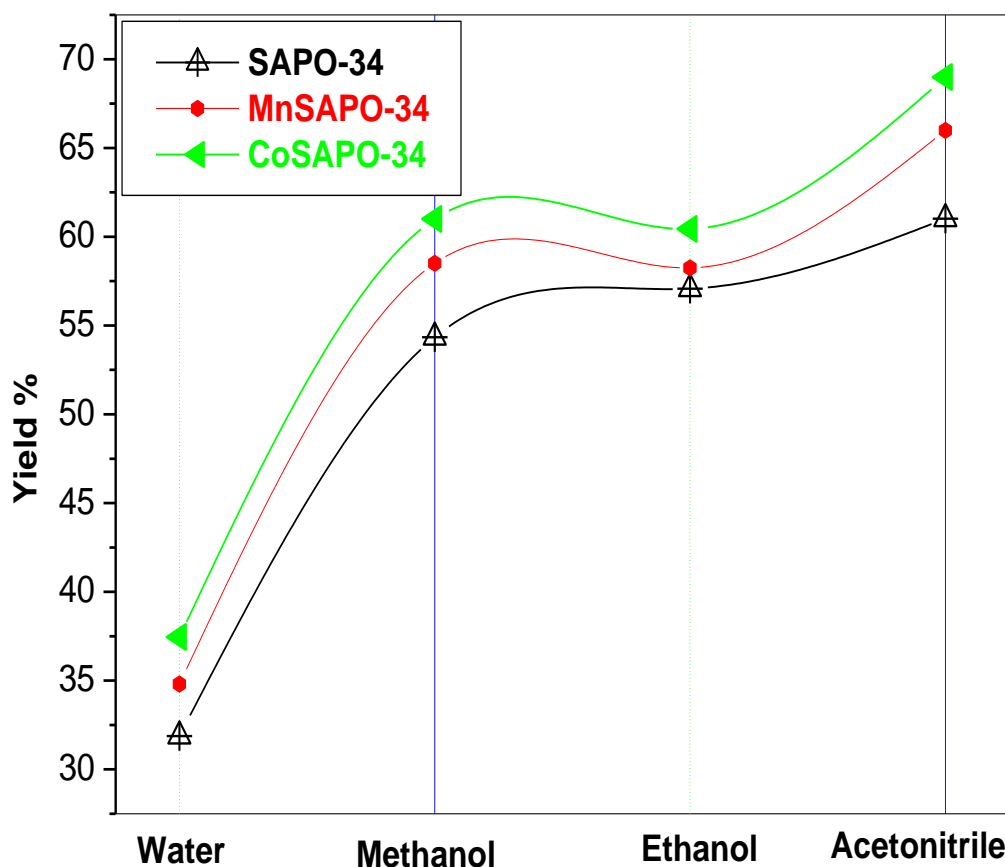
Solvent	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
Water	30.29	33.30	35.88
Methanol	36.37	57.60	61.28
Ethanol	41.63	61.25	65.47
Acetonitrile	47.02	69.25	72.02



Graph 4.1.1.5(b) Effect of different solvents on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AlPO-5

Table 4.1.1.5(c). Effect of different solvents on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34

Solvent	% yield of catalytic forms		
	SAPO-34	MnAPO-34	CoAPO-34
Water	31.88	34.81	37.45
Methanol	54.34	58.51	61.00
Ethanol	57.08	58.25	60.44
Acetonitrile	61.02	65.99	68.99



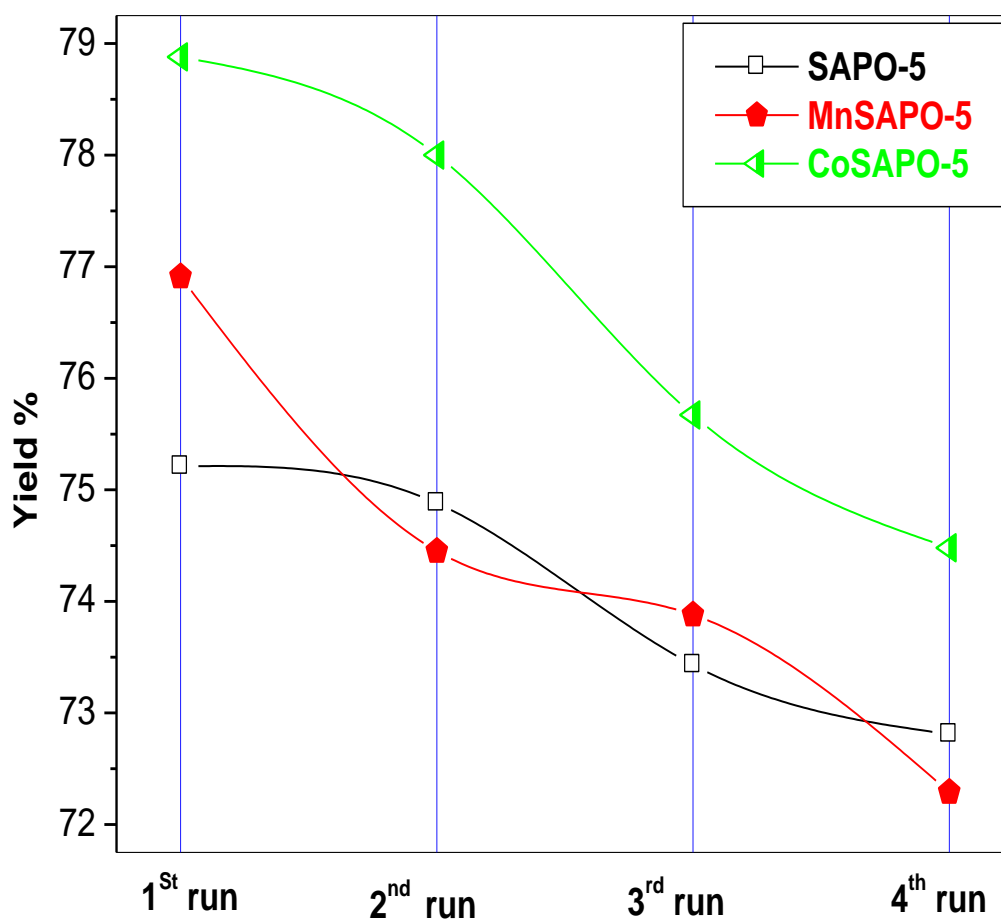
Graph 4.1.1.5(c). Effect of different solvents on yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34

#### 4.1.1.6 Catalyst recycling

Since these catalysts are solids thus are recyclable too. These catalysts were recycled and again used in the same reaction following the scheme 2.5.1. Recycling experiments for the catalysts were conducted to find out their stability of the catalysts after the reaction. Leaching of catalytic sites occur in the solid supported catalysts which make them applicable of limited reuse. However in case of metal substituted aluminophosphates and silicoaluminophosphates acidic sites are not an adsorbed one, rather they are generated intrinsically due to special type of bonding and generation of unbalanced charge on oxygen to which a proton is attached which acts as an acidic site in these materials. Thus this type of acidity is a permanent and an inherent property. However, catalyst cocking may occur in which thin surface of reactants get adsorbed on the surface of catalyst and catalyst may lose its catalytic property reasonably. Results reveal that the catalysts can be recycled several times without much loss in their activity which is clear from tables 4.1.1.6(a-c) and graphs 4.1.1.6(a-c). Catalysts were washed by ethanol after their successive use in each reaction.

Table 4.1.1.6(a). Effect of catalyst recycling on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

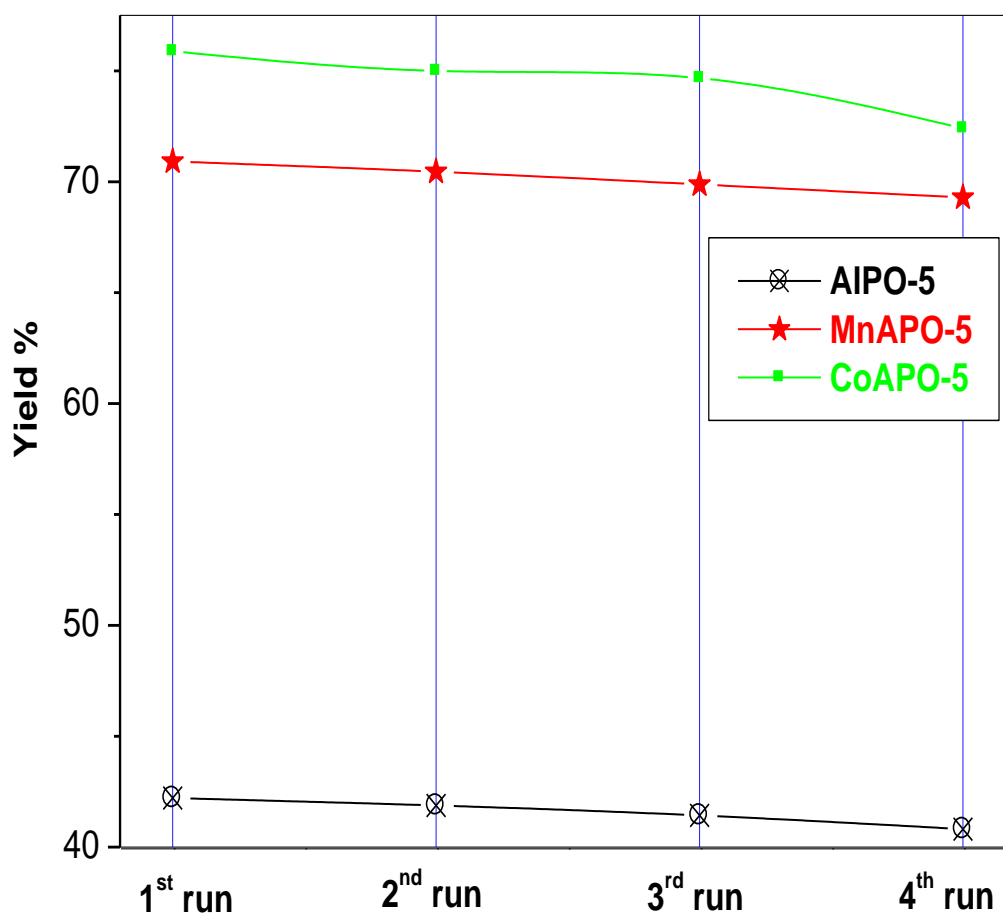
Runs	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
1 <sup>st</sup> run	75.21	76.91	78.88
2 <sup>nd</sup> run	74.88	74.45	78.00
3 <sup>rd</sup> run	73.43	73.88	75.67
4 <sup>th</sup> run	72.81	72.29	74.48



Graph 4.1.1.6(a). Effect of catalyst recycling on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-5

Table 4.1.16(b). Effect of catalyst recycling on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AIPO-5

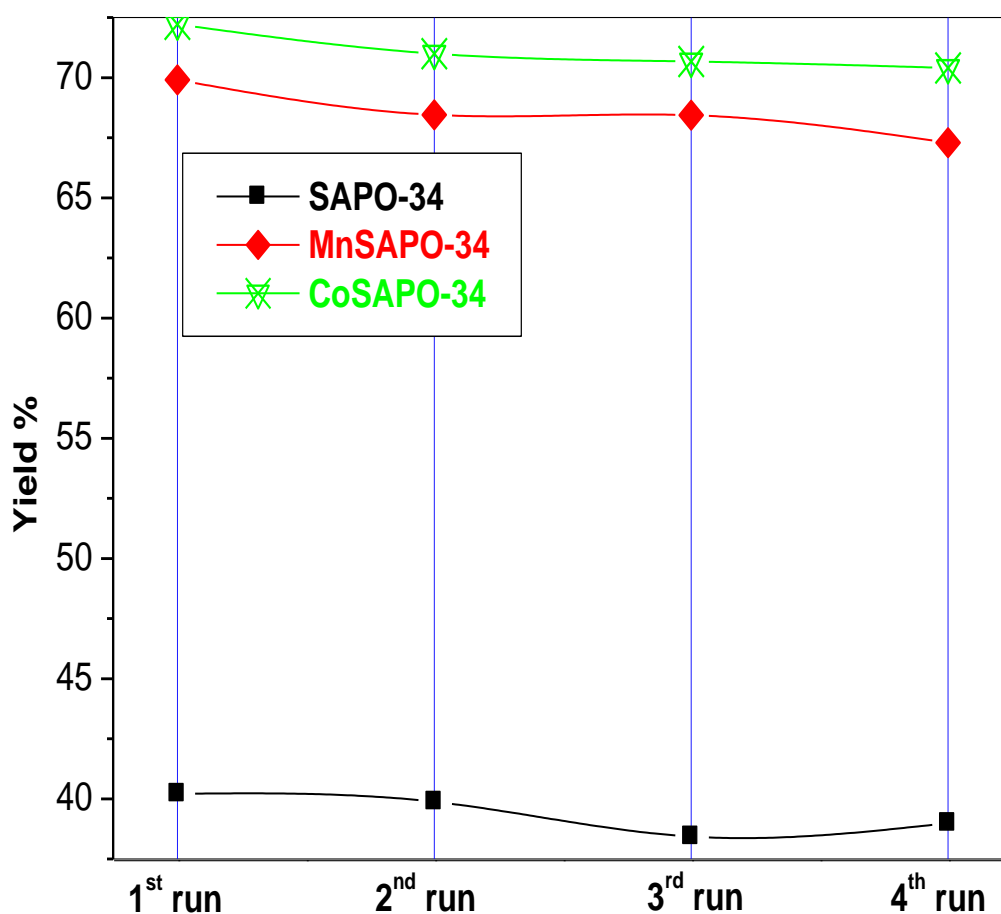
Runs	% yield of catalytic forms		
	AIPO-5	MnAPO-5	CoAPO-5
1 <sup>st</sup> run	42.21	70.91	75.88
2 <sup>nd</sup> run	41.88	70.45	75.00
3 <sup>rd</sup> run	41.43	69.88	74.67
4 <sup>th</sup> run	40.81	69.29	72.40



Graph 4.1.16(b). Effect of catalyst recycling on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of AIPO-5

Table 4.1.1.6(c). Effect of catalyst recycling on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34

Runs	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
1 <sup>st</sup> run	40.21	69.91	72.22
2 <sup>nd</sup> run	39.88	68.45	71.00
3 <sup>rd</sup> run	38.43	68.44	70.67
4 <sup>th</sup> run	38.99	67.29	70.40

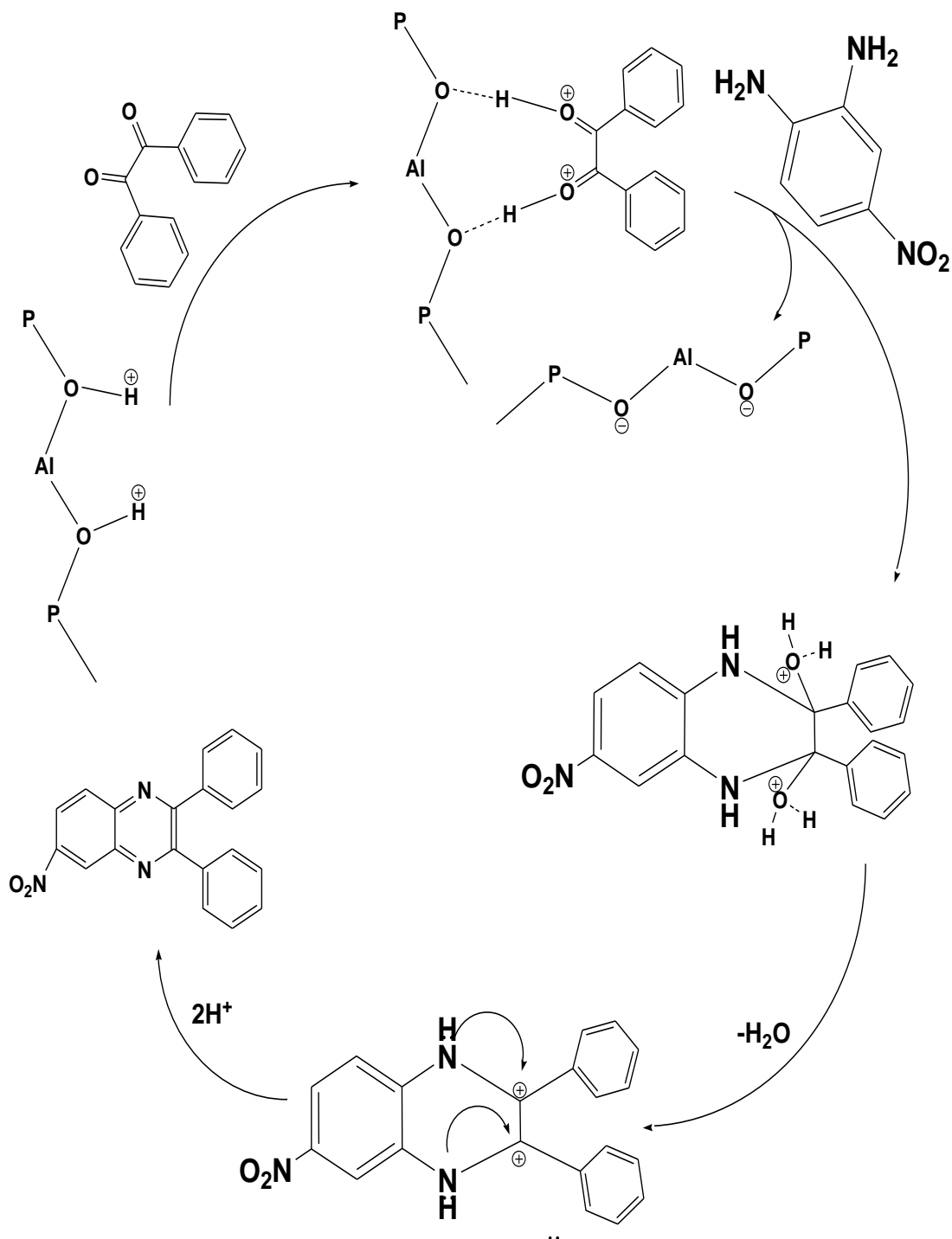


Graph 4.1.1.6(c). Effect of catalyst recycling on the yield of 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol over various catalytic forms of SAPO-34



### 4.1.2 Synthesis of 6-nitro-2,3-diphenylquinoxaline (Quinoxaline)

6-nitro-2,3-diphenylquinoxaline is of multiple use in chemistry. For instance this compound and its derivatives play a role in photochemical reactions, dyes, drugs, enzyme inhibition activities and various other uses in pharmaceutical reactions. Mechanism of this reaction is as follows.



Mechanism of quinoxaline synthesis over zeotype catalyst

Various strategies have been made using various catalysts and different reactants with one step to multi step approaches. Generally two component and single step reactions have been widely discussed in the literature which has been covered in the previous chapter in this thesis.

This compound is smaller than 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol thus the study of this compound (6-nitro-2,3-diphenylquinoxaline) will be helpful in observing effect of host-guest interaction inside solid porous catalyst material and interaction between reactants and product.

#### **4.1.2.1 Effect of different catalysts on the yield of Quinoxaline**

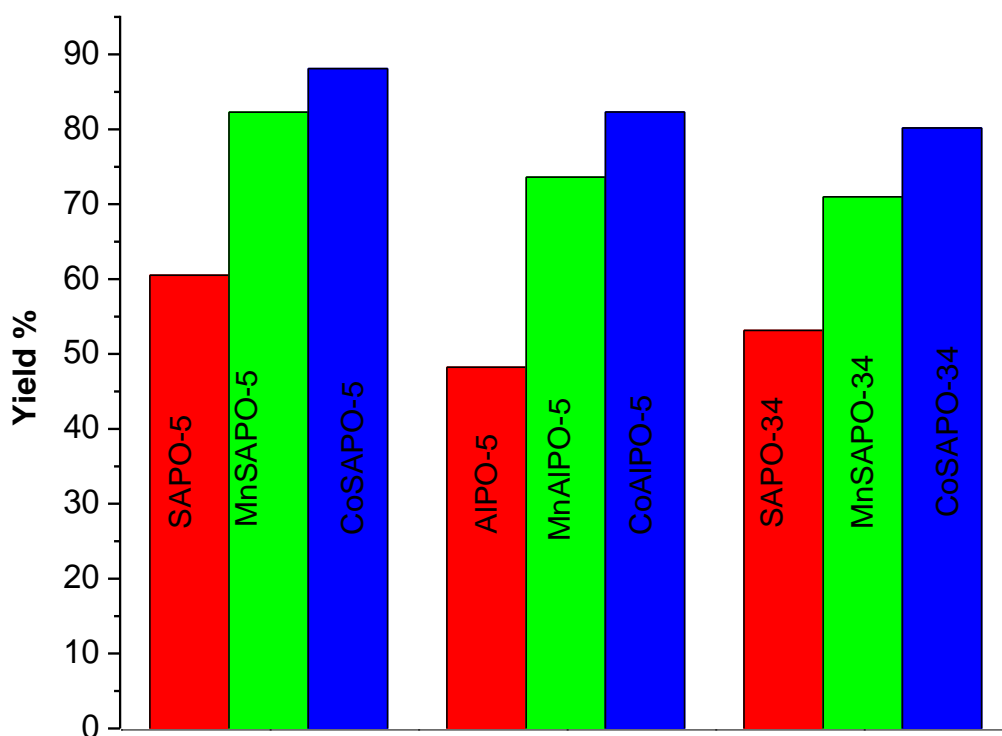
All catalyst materials with their metal analogues were tested in this reaction of 6-nitro-benzene-1,2-diamine, and benzil. Reaction conditions were followed according to the scheme 2.5.2. Yield was calculated on the basis of isolated product weight. TLC plate was developed using ethanol to monitor the reaction progress continuously. During the reaction, initially, colour of the reaction mixture remained red but as the reaction proceeds forward, light brown colour appears followed by formation of a precipitate of product which was then separated out from the reaction mixture and dried in oven after re-crystallization in ethanol.

#### 4.1.2.1 Effect of various forms of catalysts on the yield of 6-nitro-2,3-diphenylquinoxaline

Effect of different catalytic forms of catalysts is given in the following table 4.1.2.1 and graph 4.1.2.1.

**Table 4.1.2.1. Effect of different catalytic forms of catalysts on the yield of 6-nitro-2,3-diphenylquinoxaline**

Catalyst form	% yield of catalytic forms		
	SAPO-5	AIPO-5	SAPO-34
Non Substituted	60.53	48.23	53.14
Mn <sup>2+</sup> Substituted	82.29	73.61	70.99
Co <sup>2+</sup> Substituted	88.11	82.30	80.19



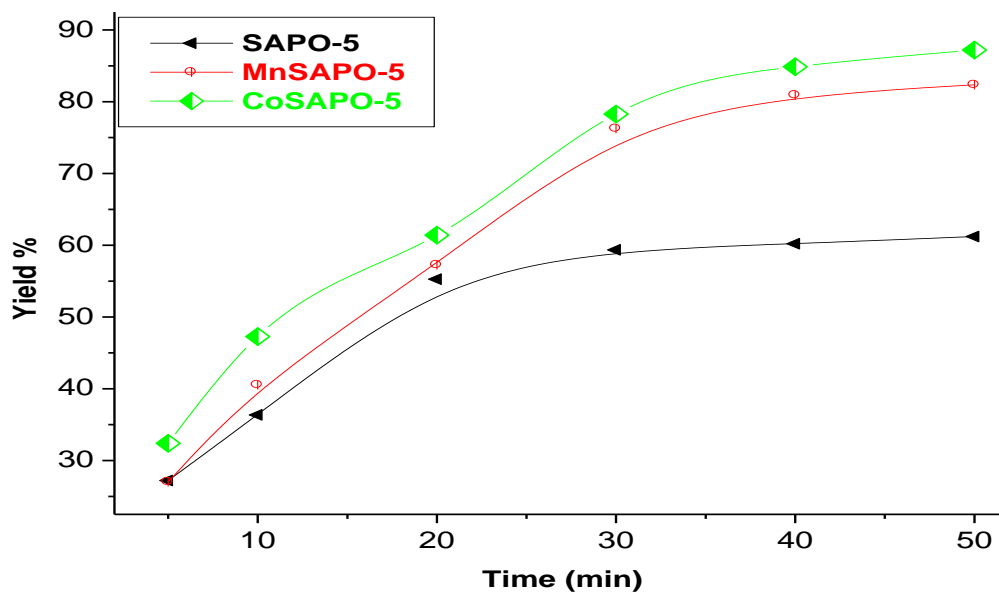
Graph 4.1.2.1. Effect of various catalytic forms of catalysts on the yield of 6-nitro-2,3-diphenylquinoxaline

#### 4.1.2.2 Effect of reaction time

Effect of reaction time was studied over a reasonable time scale following the reaction procedure and variables as described in the previous chapter in scheme 2.5.2. The results obtained for all different catalysts are listed below in tables 4.1.2.2(a-c) and graph 4.1.2.2(a-c).

**Table 4.1.2.2(a). Effect of reaction time on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5**

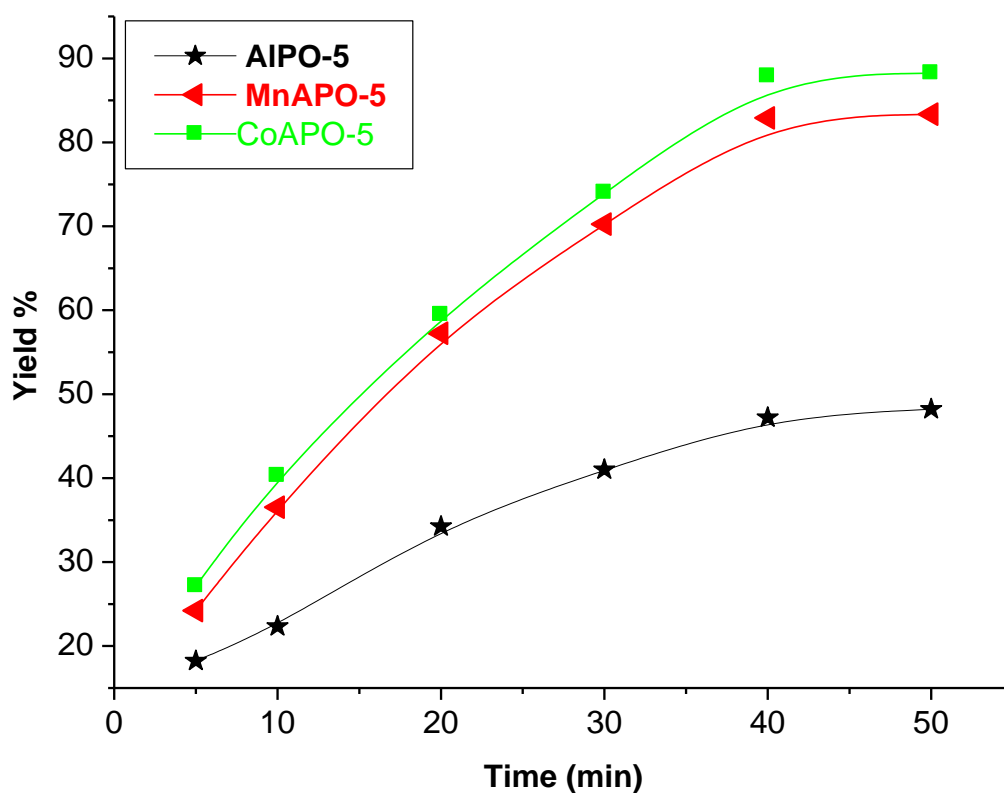
Time (min)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
5	27.22	27.02	32.4
10	36.36	40.71	47.02
20	44.28	51.85	61.99
30	51.36	60.25	71.29
40	53	70.58	80.25
50	54.22	72.00	81.26



Graph 4.1.2.2(a). Effect of reaction time on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5

Table 4.1.2.2-b. Effect of reaction time on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AIPO-5

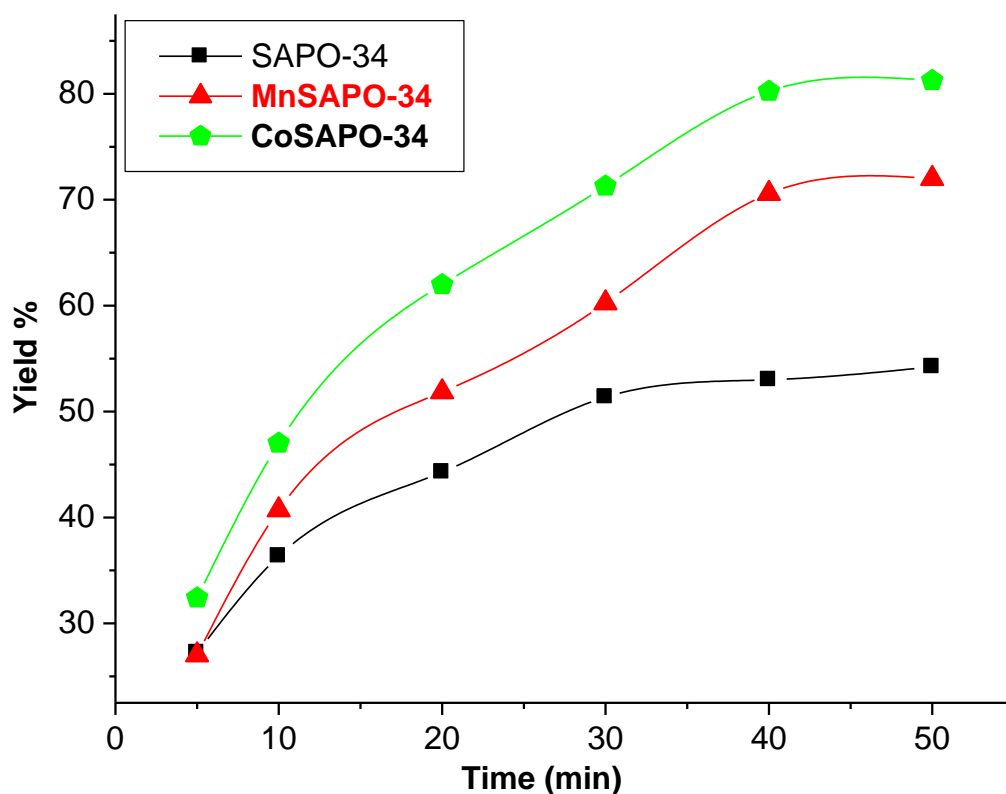
Time (min)	% yield of catalytic forms		
	AIPO-5	MnAPO-5	CoAPO-5
5	18.22	24.22	27.14
10	22.34	36.54	40.28
20	34.24	57.25	59.47
30	41.02	70.25	74.02
40	47.21	82.91	87.88
50	48.22	83.35	88.24



Graph 4.1.2.2(b). Effect of reaction time on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AIPO-5

Table 4.1.2.2(c). Effect of reaction time on the yield of 6-nitro-2,3-diphenyl quinoxaline over various catalytic forms of SAPO-34

Time(min)	% yield of catalytic forms		
	SAPO-34	MnAPO-34	CoAPO-34
5	24.21	31.81	35.00
10	36.34	48.51	49.00
20	52.08	58.25	56.44
30	61.02	68.99	71.99
40	62.28	71.41	72.20
50	73.29	71.35	73.99



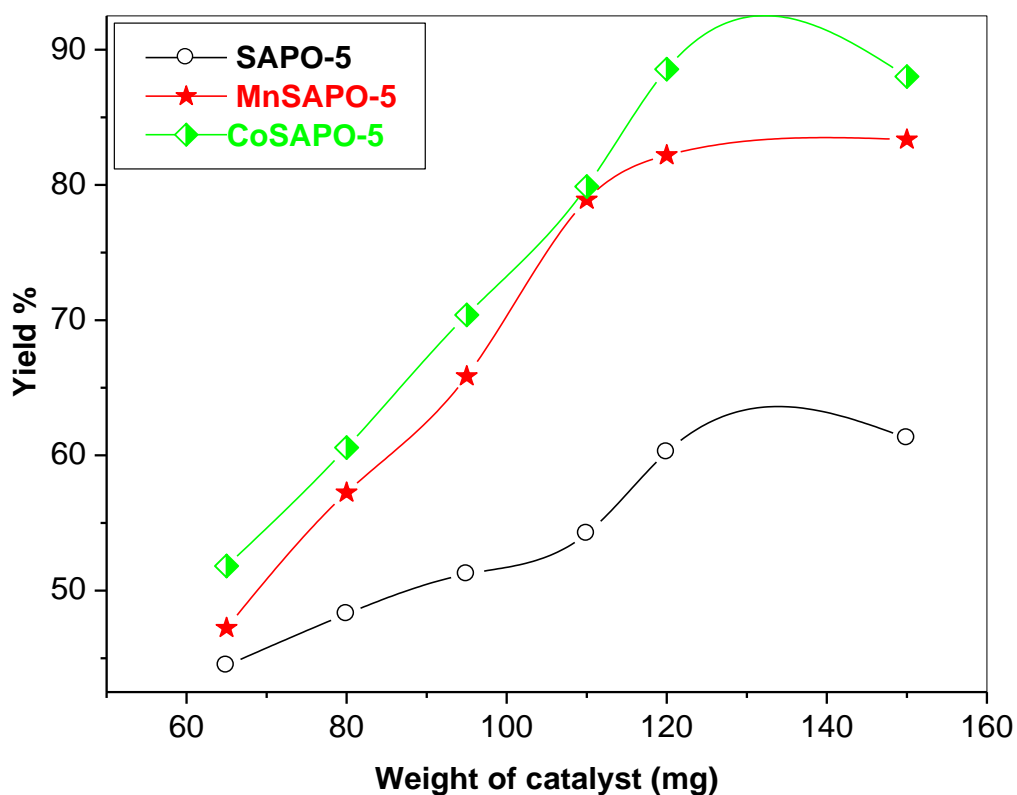
Graph 4.1.2.2(c). Effect of reaction time on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

#### 4.1.2.3 Effect of weight of catalyst

To study the effect of amount of catalyst, weight of the catalyst was changed keeping all the other synthesis variables constant. Reaction was followed according to the scheme 2.5.2. The results obtained for this variable are straight and yield of product is proportional to the weight of catalyst employed in the corresponding reaction. Catalyst weight was varied over a reasonable range of weight that is 50-150 mg. As the reaction was performed in a little aliquot of reactants, this range of catalyst weight was reasonable. In the reaction which is performed according to the scheme 2.5.2, different solvents were taken and catalyst was shaken in solvent before mixing all reagents. It is observed that as the amount of catalyst increases, the yield of product also increases. But after 120 mg amount of the catalyst reaction rate does not increase in a proportional way and also causes impurities due to the reactants which remain unreacted observed in TLC plate. Results obtained for different catalysts are listed in the table 4.1.2.3 (a-c) and graph (a-c).

Table 4.1.2.3(a). Effect of weight of catalyst on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5

Weight (mg)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
65	44.47	47.24	51.82
80	48.28	57.25	60.58
95	51.22	65.85	70.38
110	54.21	78.91	79.88
120	60.24	82.20	88.56
150	61.28	83.35	88.01

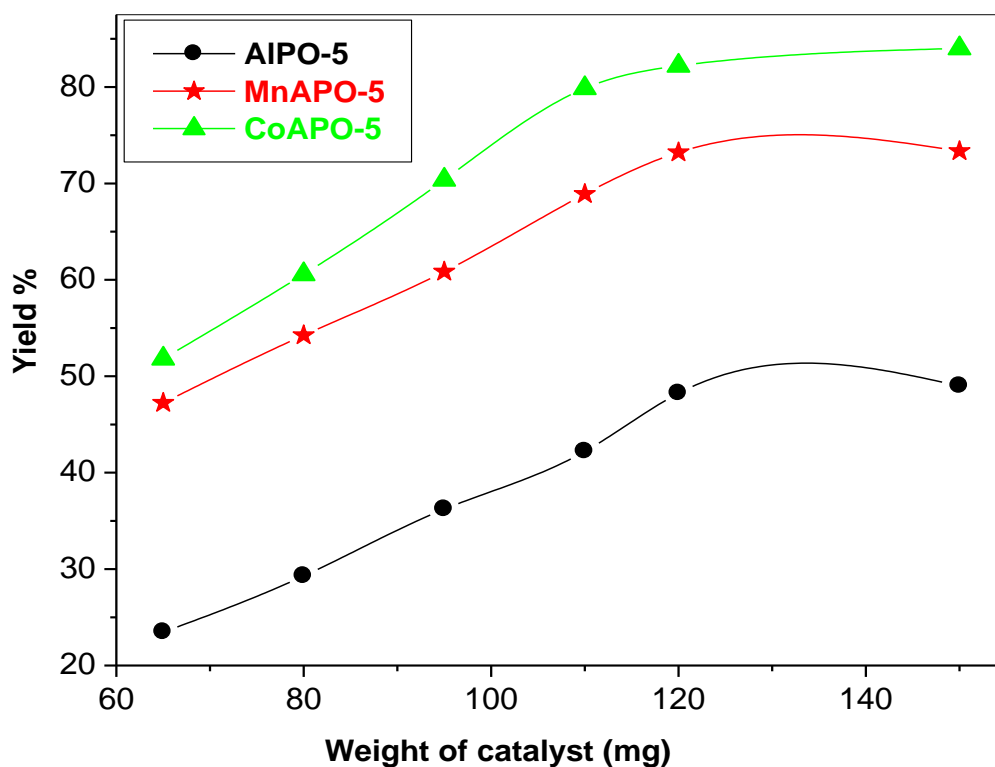


Graph 4.1.2.3(a). Effect of weight of catalyst on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5



Table 4.1.2.3(b). Effect of weight of catalyst on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AlPO-5

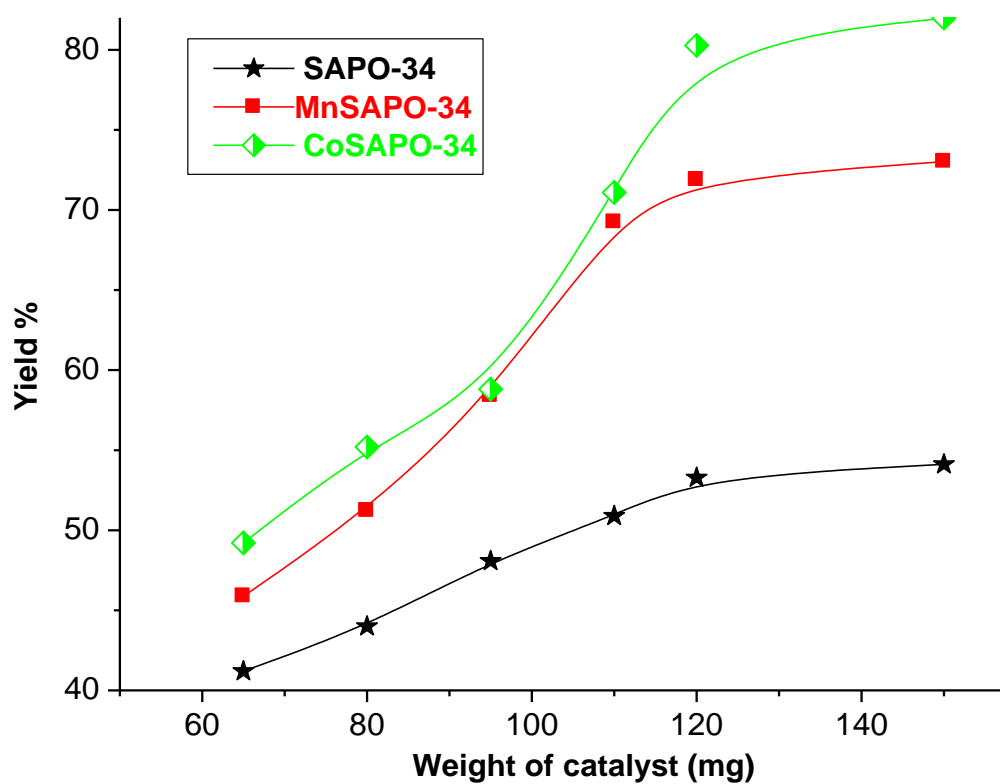
Weight (mg)	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
65	23.47	47.24	51.82
80	29.28	54.25	60.58
95	36.22	60.85	70.38
110	42.21	68.91	79.88
120	48.24	73.22	82.20
150	49.00	73.35	84.01



Graph 4.1.2.3(b). Effect of weight of catalyst on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AlPO-5

Table 4.1.2.3(c). Effect of weight of catalyst on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

Weight (mg)	% yield of catalytic forms		
	SAPO-34	MnAPO-34	CoAPO-34
65	41.20	45.88	49.21
80	44.00	51.22	55.20
95	48.08	58.39	58.81
110	50.89	69.24	71.09
120	53.28	71.88	80.28
150	54.12	73.02	81.98



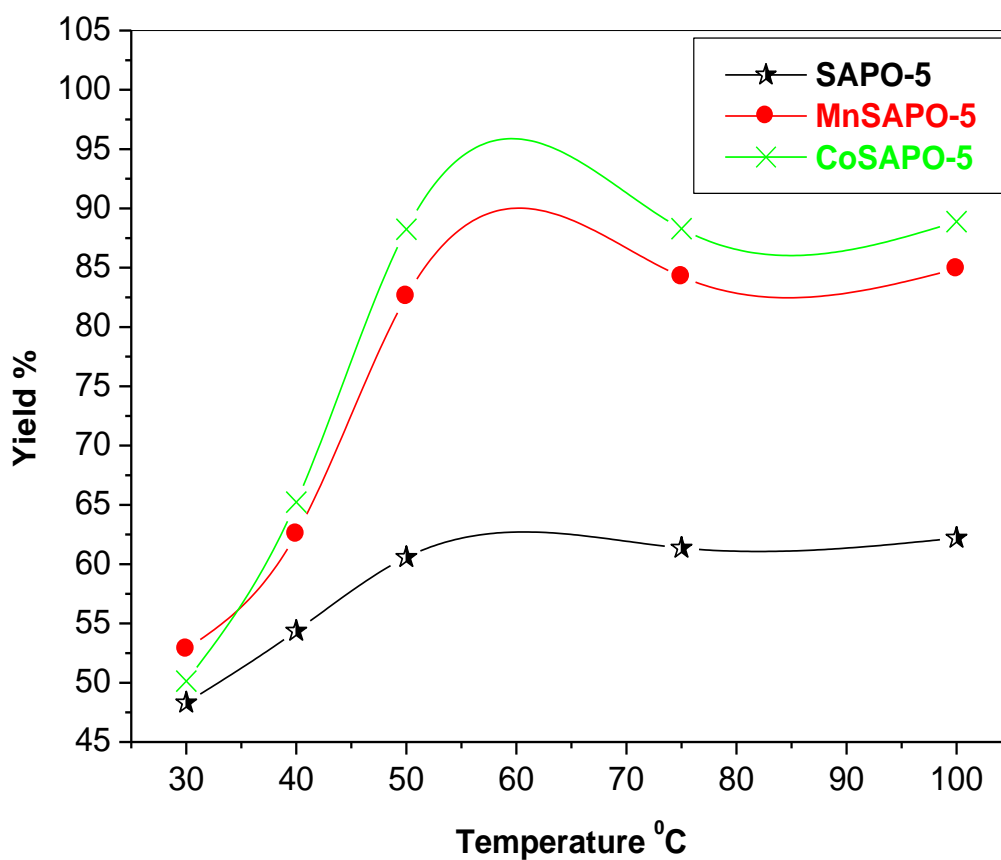
Graph 4.1.2.3(c). Effect of weight of catalyst on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

#### 4.1.2.4 Effect of reaction temperature

Effect of reaction temperature was studied over a range of temperature (30-100°C) for the synthesis of 6-nitro-2,3-diphenylquinoxaline, following the same reaction conditions explained in the scheme 2.2.5. All other synthesis variables were kept constant except temperature which was varied for different reaction batches. It was found that reaction temperature has an impact on the yield of products however reaction proceeds at relatively low temperature efficiently. The results for this variable are given in the tables 4.1.2.4(a-c). and graphs 4.1.2.4(a-c). The presence of -NO<sub>2</sub>, causes de-stabilization of ring electron on benzene, thus has an impact on chemical reactivity with catalysts. Most efficient temperature was found to be around 50 °C.

Table 4.1.2.4(a). Effect of reaction temperature on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5

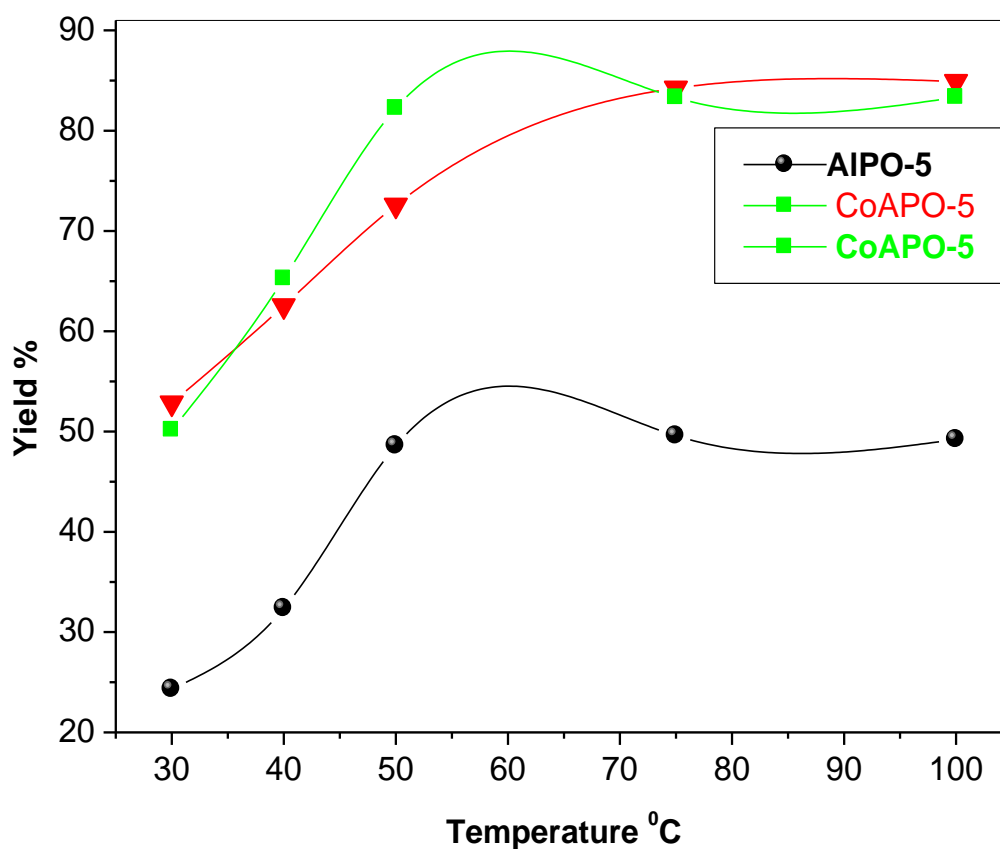
Temperature (°C)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
30	48.31	52.84	50.14
40	54.36	62.54	65.23
50	60.58	82.58	88.24
75	61.36	84.25	88.29
100	62.21	84.91	88.88



Graph 4.1.2.4(a) Effect of reaction temperature on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5

Table 4.1.2.4(b). Effect of reaction temperature on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AlPO-5

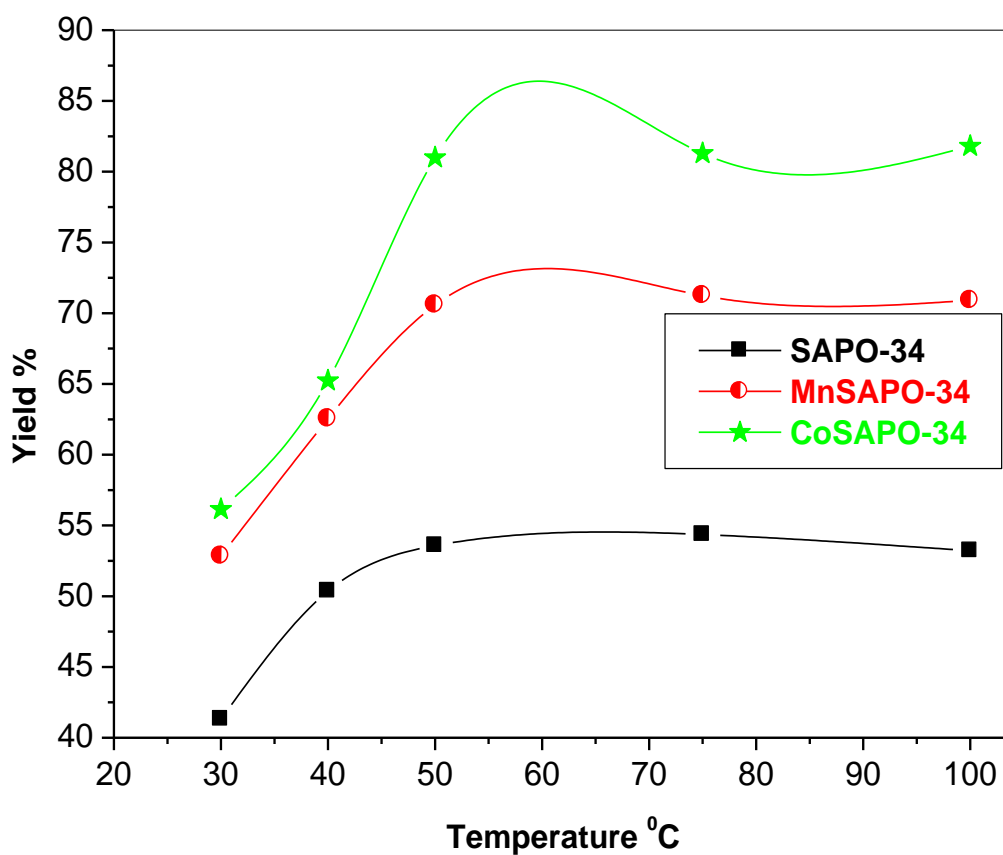
Temperature (°C)	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
30	24.32	52.84	50.14
40	32.36	62.54	65.23
50	48.58	72.58	82.24
75	49.58	84.25	83.29
100	49.21	84.91	83.34



Graph 4.1.2.4(b). Effect of reaction temperature on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AlPO-5

Table 4.1.2.4(c). Effect of reaction temperature on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

Temperature (°C)	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
30	41.31	52.84	56.14
40	50.36	62.54	65.23
50	53.58	70.58	80.99
75	54.36	71.25	81.29
100	53.21	70.91	81.81



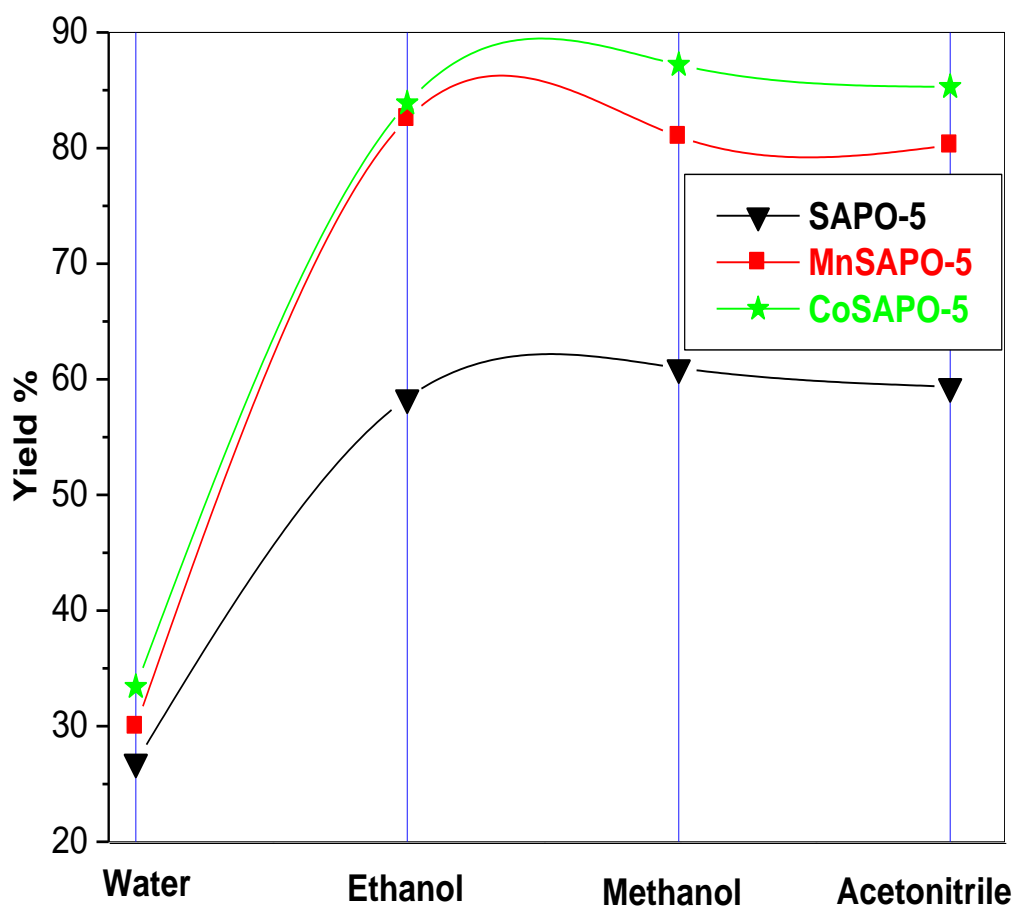
Graph 4.1.2.4(c). Effect of reaction temperature on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

#### 4.1.1.5 Effect of different solvents

Effect of different solvents on the synthesis of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of aluminophosphate and silicoaluminophosphate was studied. The reaction for the synthesis of 6-nitro-2,3-diphenylquinoxaline was performed basically without solvent and the results for product yield were excellent. To examine the effect of solvent, the reaction was performed in different solvent system (water, ethanol, methanol and acetonitrile) following the same synthesis parameters employed in scheme 2.5.2 by keeping all other parameters constant. The results obtained for different catalysts are given in the tables 4.1.2.5(a-c) and 4.1.2.5(a-c). It is formulated that these solvents are polar in nature and may be adsorbed on the surface of polar zeotypes, as these catalysts are having free hydroxyl groups on their surface. Hydrogen bonding and chemisorption of these polar solvents on the surface of catalysts may create a competition between the reactant molecules which are of organic origin and bigger in size. Thus, there is a possibility of adsorption of solvents first on the surface of catalysts than the reactants thus equilibrium will shift towards the solvents followed by the decrease in the obtained surface area for the reactants. However in comparison to the Imidazole synthesis interaction between catalyst and different solvent molecules is less effective. There may be two reasons behind it. First is size of 6-nitro-2,3-diphenylquinoxaline molecule which is smaller than Imidazole and second is the presence of nitro group on the reactant which makes it a polar molecule. Thus, the overall effect of these two reasons leads to relatively higher yield of 6-nitro-2,3-diphenylquinoxaline because the reactant molecules get adsorbed first on the surface of the catalyst than that of solvent molecule. Thus overall effect makes this reaction to be completed comparatively at low temperature and greater yield than Imidazole.

Table 4.1.2.5(a). Effect of different solvents on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5

Solvent	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
Water	26.88	29.98	33.41
Methanol	58.38	82.54	83.88
Ethanol	60.99	81.00	87.21
Acetonitrile	59.36	80.25	85.29

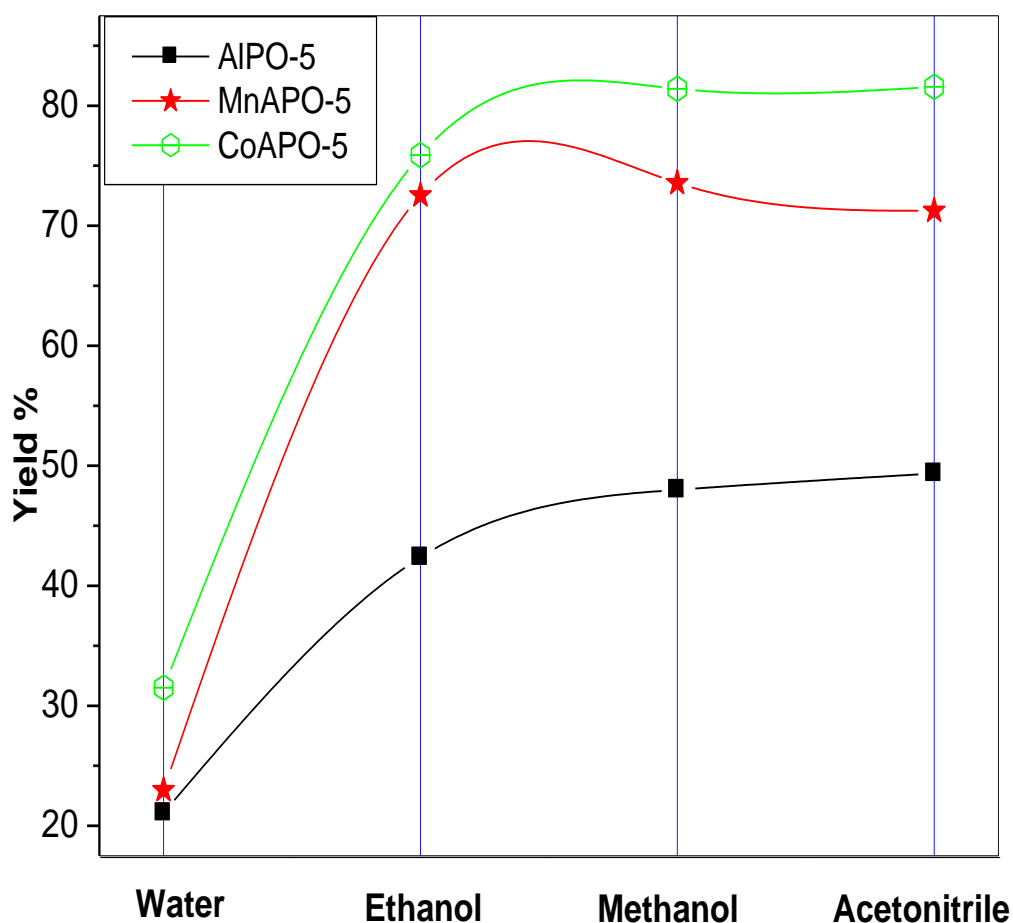


Graph 4.1.2.5(a). Effect of different solvents on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5



Table 4.1.2.5(b). Effect of different solvents on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AIPO-5

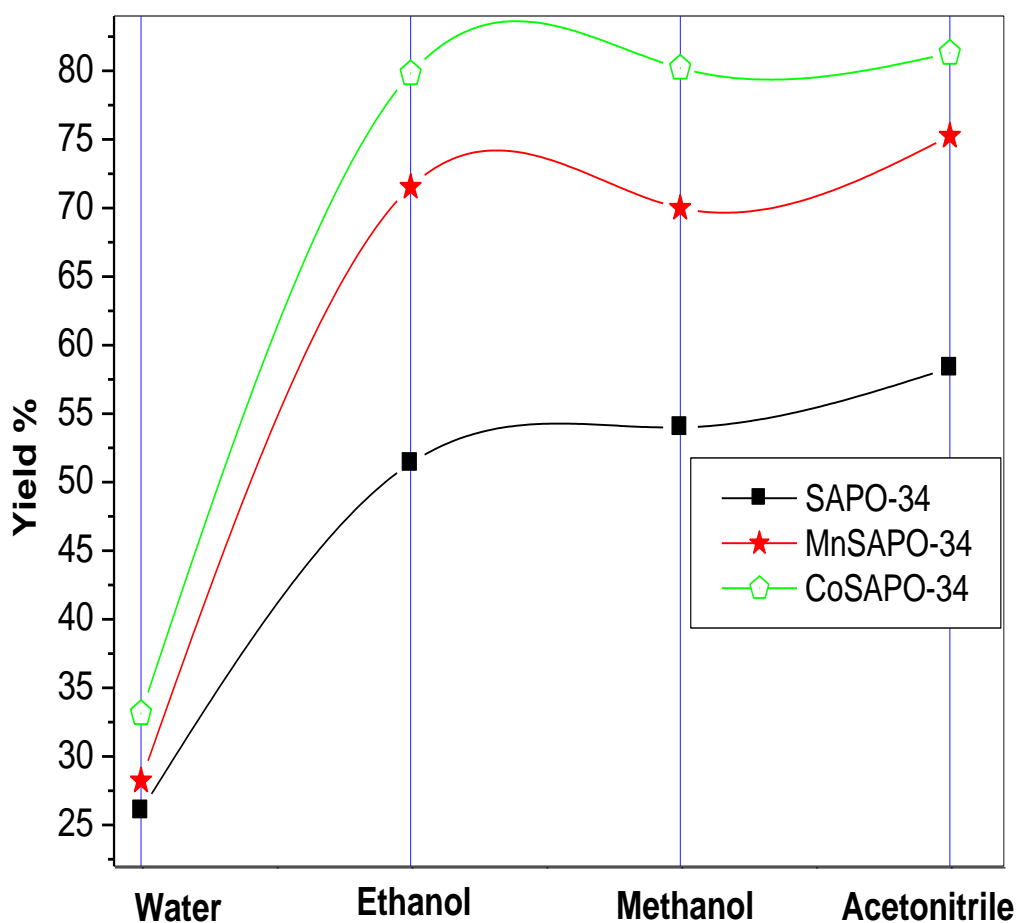
Solvent	% yield of catalytic forms		
	AIPO-5	MnAPO-5	CoAPO-5
Water	21.07	22.98	31.51
Methanol	42.38	72.54	75.88
Ethanol	48.25	73.56	81.41
Acetonitrile	49.36	71.25	81.57



Graph 4.1.2.5(b). Effect of different solvents on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AIPO-5

Table 4.1.2.5(c). Effect of different solvents on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

Solvent	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
Water	26.04	28.23	33.14
Methanol	51.38	71.54	79.80
Ethanol	53.99	70.00	80.21
Acetonitrile	58.34	75.25	81.29

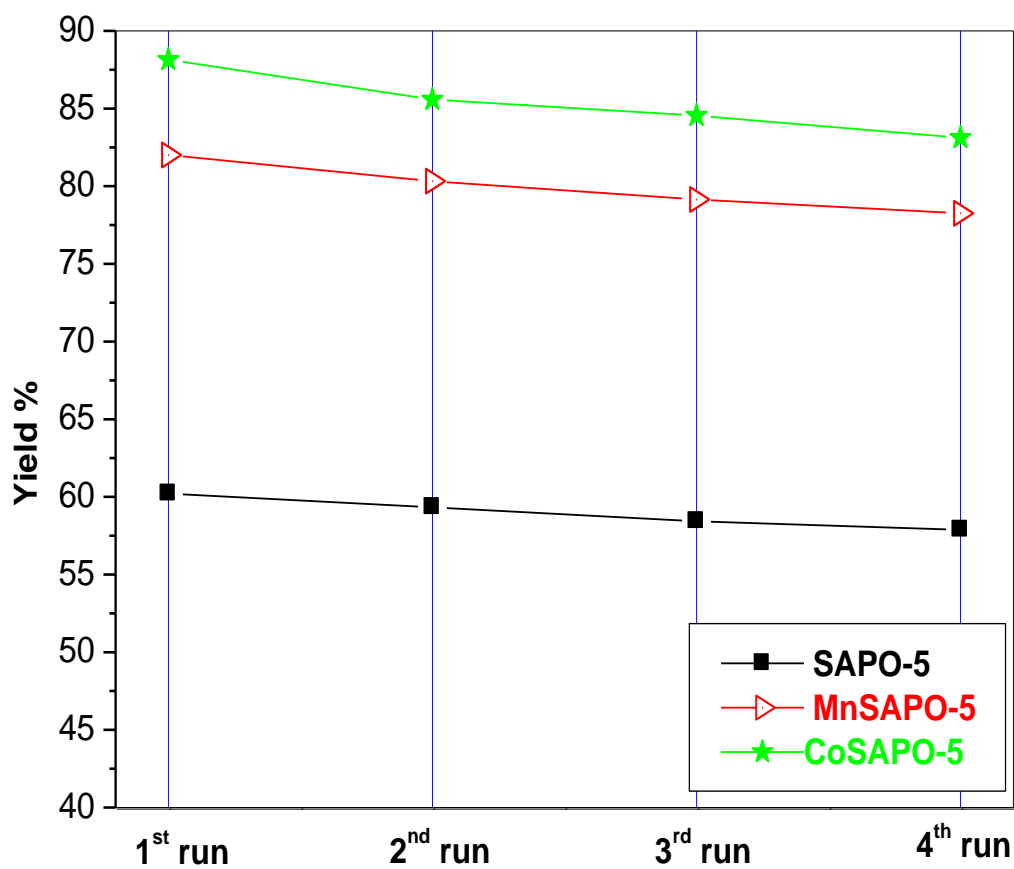


Graph 4.1.2.5(c). Effect of different solvents on percentage yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

## 4.1.2.6 Effect of catalyst recycling

Table 4.1.2.6(a). Effect of catalyst recycling on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5

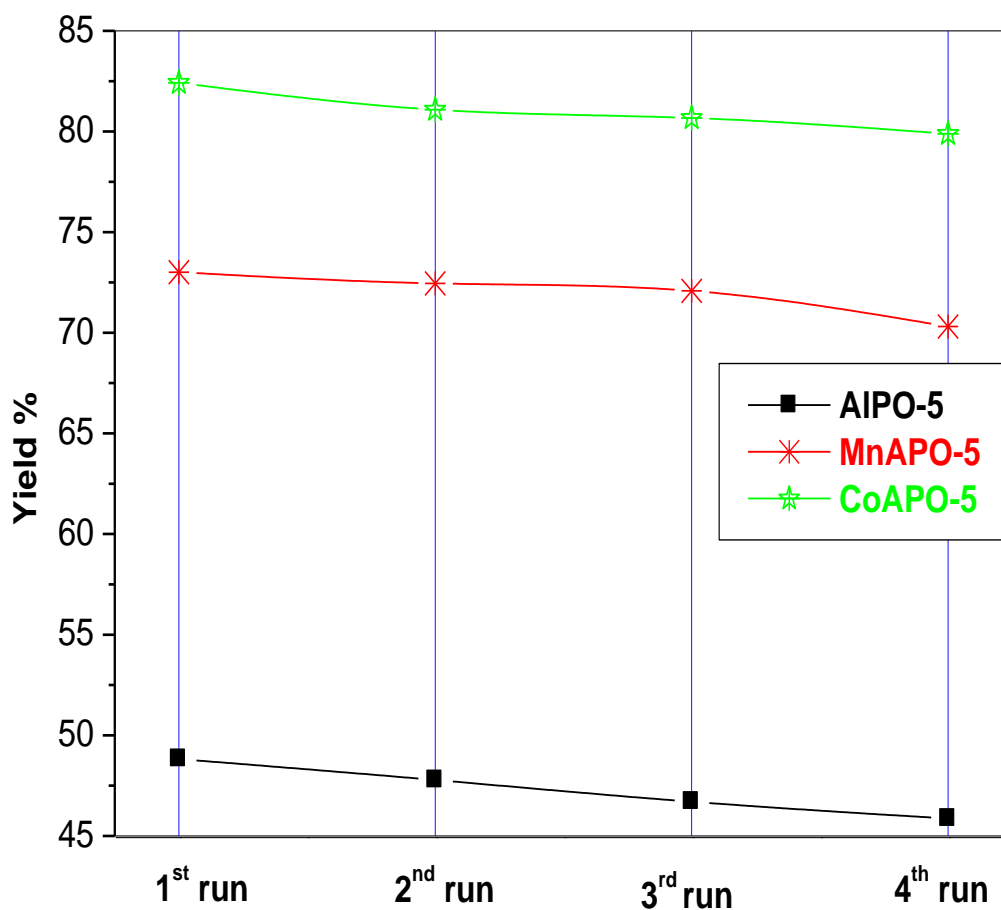
Runs	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
1 <sup>st</sup> run	60.21	82.01	88.14
2 <sup>nd</sup> run	59.33	80.33	85.58
3 <sup>rd</sup> run	58.43	79.14	84.55
4 <sup>th</sup> run	57.88	78.25	83.12



Graph 4.1.2.6(a). Effect of catalyst recycling on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-5

Table 4.1.2.6(b). Effect of catalyst recycling on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AIPO-5

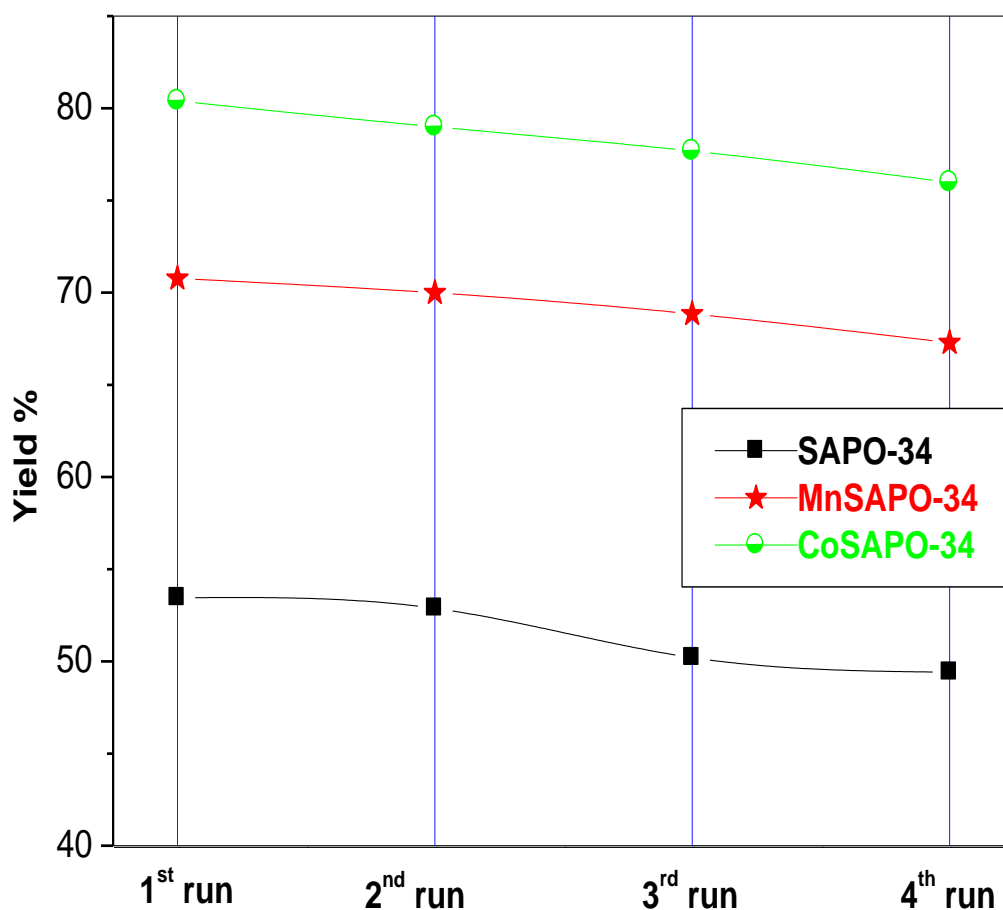
Runs	% yield of catalytic forms		
	AIPO-5	MnAPO-5	CoAPO-5
1 <sup>st</sup> run	48.82	73.01	82.42
2 <sup>nd</sup> run	47.78	72.45	81.08
3 <sup>rd</sup> run	46.70	72.08	80.67
4 <sup>th</sup> run	45.87	70.31	79.88



Graph 4.1.2.6(b). Effect of catalyst recycling on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of AIPO-5

Table 4.1.2.6(c). Effect of catalyst recycling on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

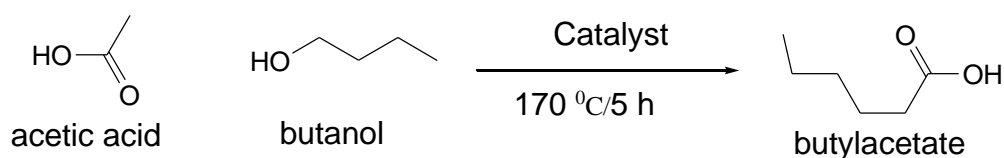
Runs	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
1 <sup>st</sup> run	53.45	70.77	80.40
2 <sup>nd</sup> run	52.88	69.99	79.00
3 <sup>rd</sup> run	50.20	68.85	77.68
4 <sup>th</sup> run	49.41	67.29	75.98



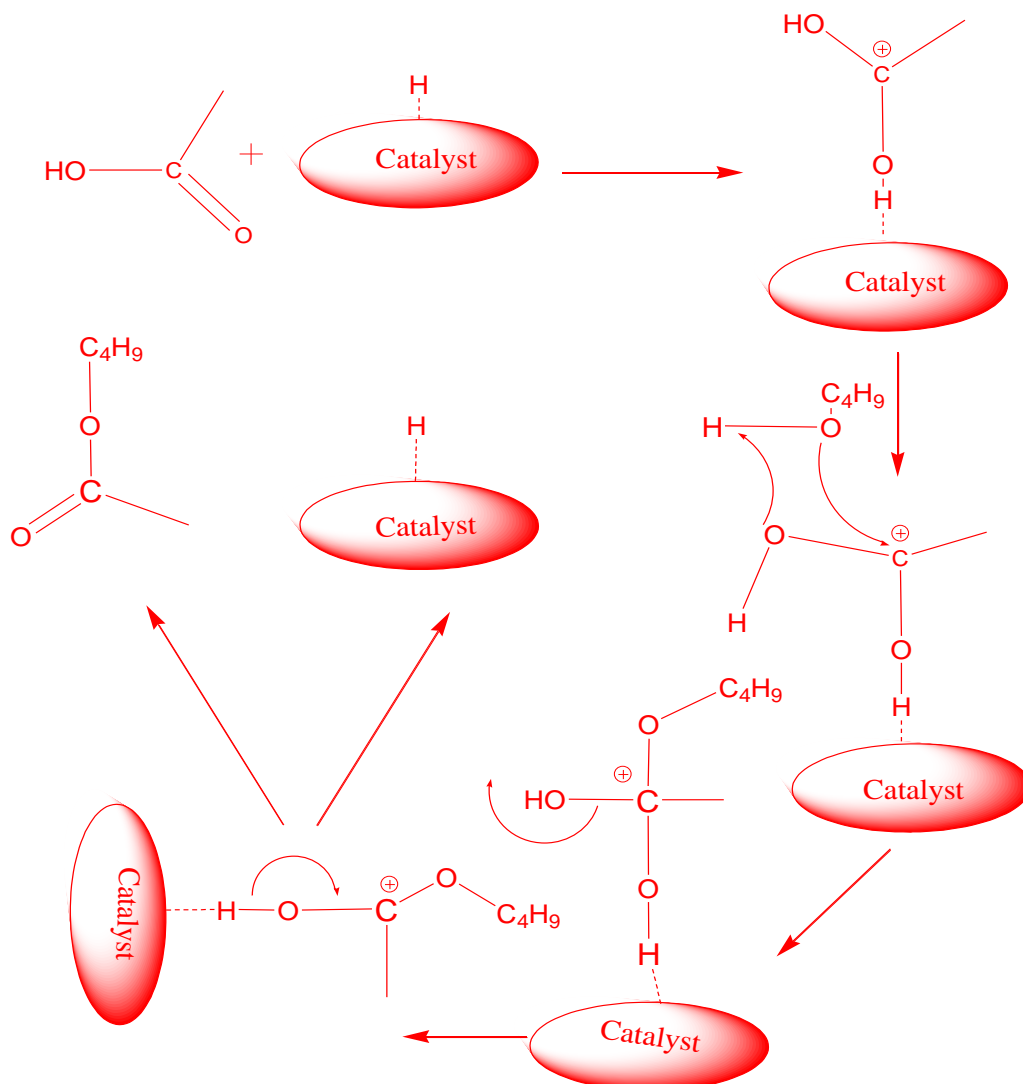
Graph 4.1.2.6(c). Effect of catalyst recycling on the yield of 6-nitro-2,3-diphenylquinoxaline over various catalytic forms of SAPO-34

### 4.1.3 Esterification reaction

Esterification of acetic acid with sec-butanol was studied over various zeotypes. The reaction products were collected from the round bottom flask and analyzed by NMR and FTIR. The catalyst was then washed with water and activated for next experiments. Reaction scheme is presented in scheme 2.5.3.



Plausible mechanism of reaction is given as follows.



**Mechanism of esterification reaction over zeotype catalyst**

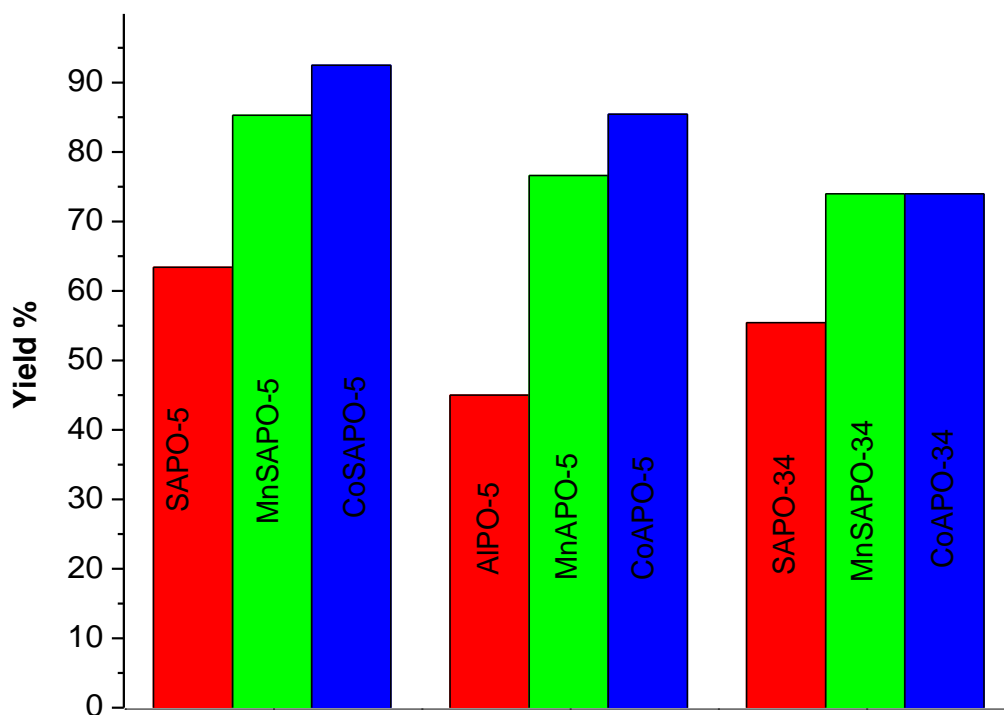
All catalyst materials with their metal analogues were tested in this esterification reaction, where synthesis conditions were followed according to the scheme 2.5.3. Effect of various synthesis variables is given as follows.

#### 4.1.3.1 Effect of different catalyst on yield of butyl acetate

Effect of different catalysts on the yield of product is given in the following table and graph 4.1.3.1.

**Table 4.1.3.1. Effect of various catalysts on the yield of butyl acetate**

Catalyst form	% yield of catalytic forms		
	SAPO-5	AIPO-5	SAPO-34
Non Substituted	63.41	45.01	55.42
Mn <sup>2+</sup> Substituted	85.29	76.61	73.99
Co <sup>2+</sup> Substituted	92.49	85.43	82.89



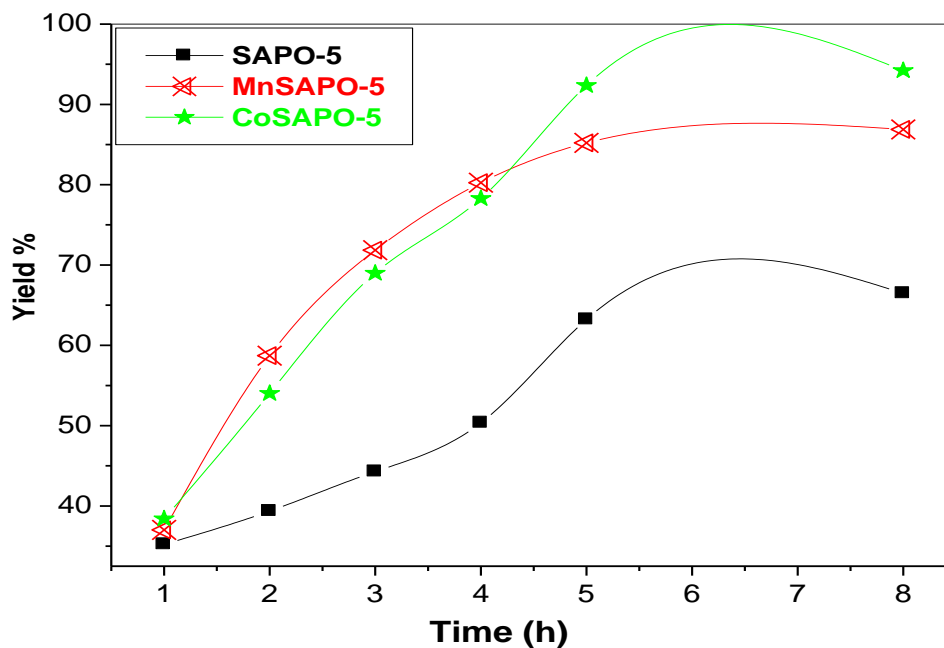
Graph 4.1.3.1. Effect of catalysts on the yield of butyl acetate

#### 4.1.3.2 Effect of reaction time

Effect of reaction was studied over a reasonable time scale following the reaction procedure and variables as described in the previous chapter in scheme 2.5.3.

**Table 4.1.3.2(a). Effect of reaction time on the yield of butyl acetate over various catalytic forms of SAPO-5**

Time (h)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
1	35.22	37.02	38.41
2	39.36	58.71	54.02
3	44.28	71.85	68.99
4	50.36	80.25	78.29
5	63.22	85.21	92.36
8	66.47	86.88	94.21

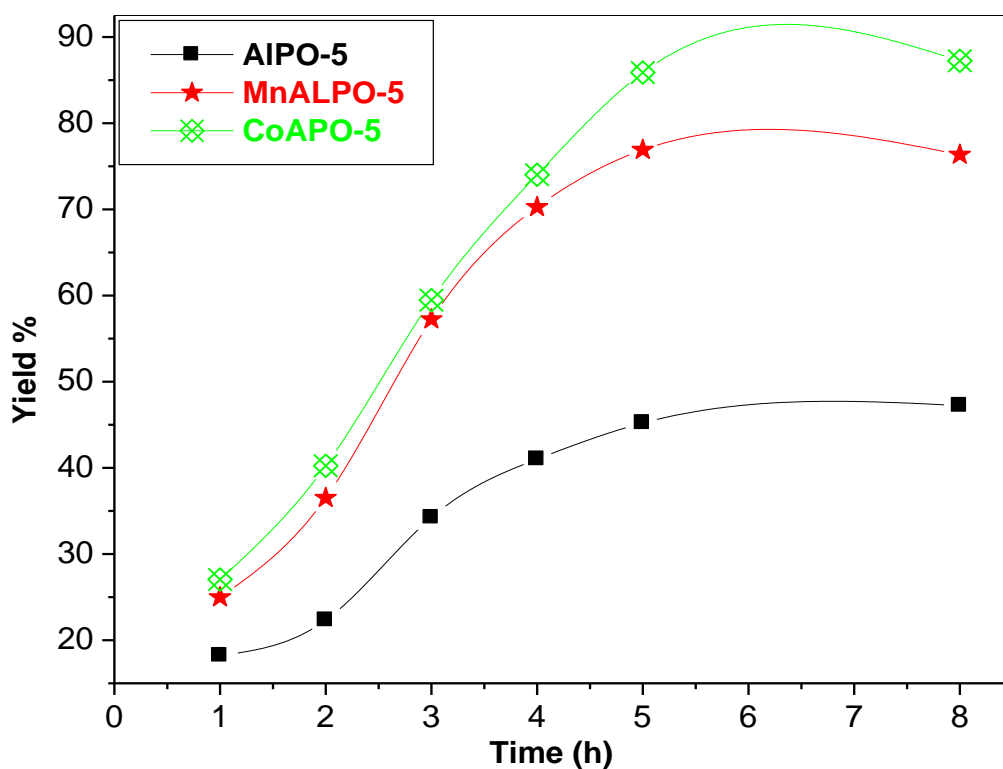


Graph 4.1.3.2(a). Effect of reaction time on the yield of butyl acetate over various catalytic forms of SAPO-5



Table 3.1.3.2(b). Effect of reaction time on the yield of butylactate over various catalytic forms of AIPO-5

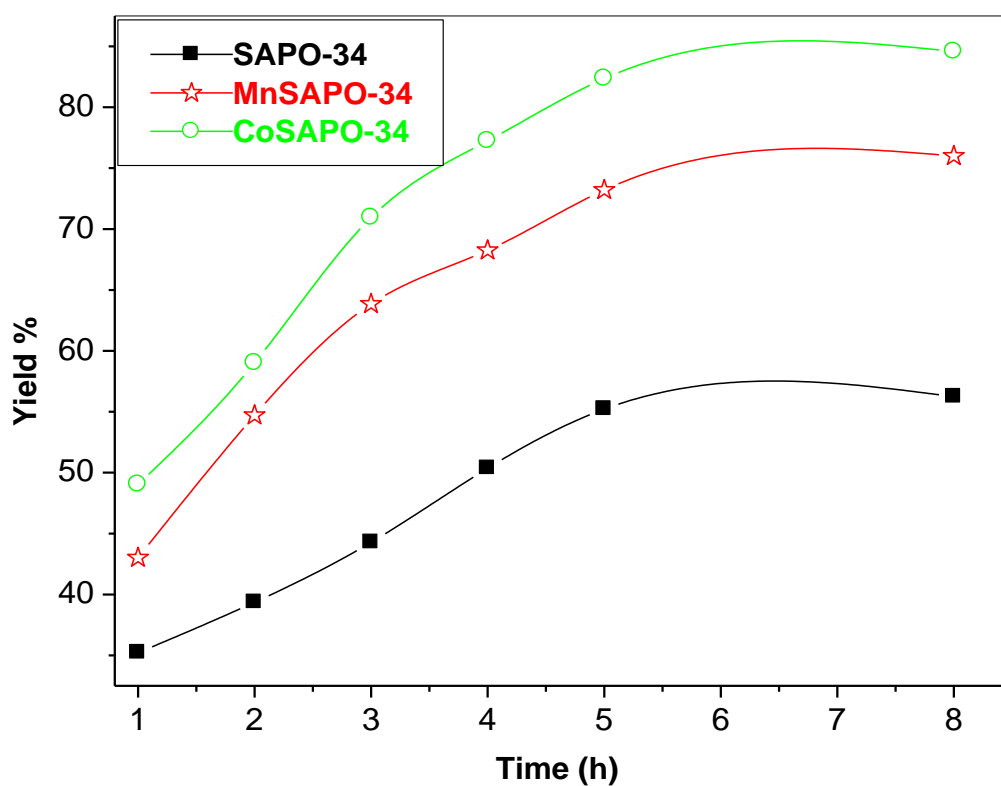
Time (h)	% yield of catalytic forms		
	AIPO-5	MnAlPO-5	CoAlPO-5
1	18.22	24.99	27.04
2	22.34	36.51	40.25
3	34.24	57.25	59.47
4	41.02	70.28	74.02
5	45.21	76.91	85.88
8	47.22	76.35	87.24



Graph 3.1.3.2(b). Effect of reaction time on the yield of butylactate over various catalytic forms of AIPO-5

Table 4.1.3.2(c). Effect of reaction time on the yield of butyl actate over various catalytic forms of SAPO-34

Time (h)	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
1	35.22	43.02	49.04
2	39.36	54.71	59.02
3	44.28	63.85	70.95
4	50.36	68.25	77.24
5	55.22	73.21	82.36
8	56.24	76.00	84.58

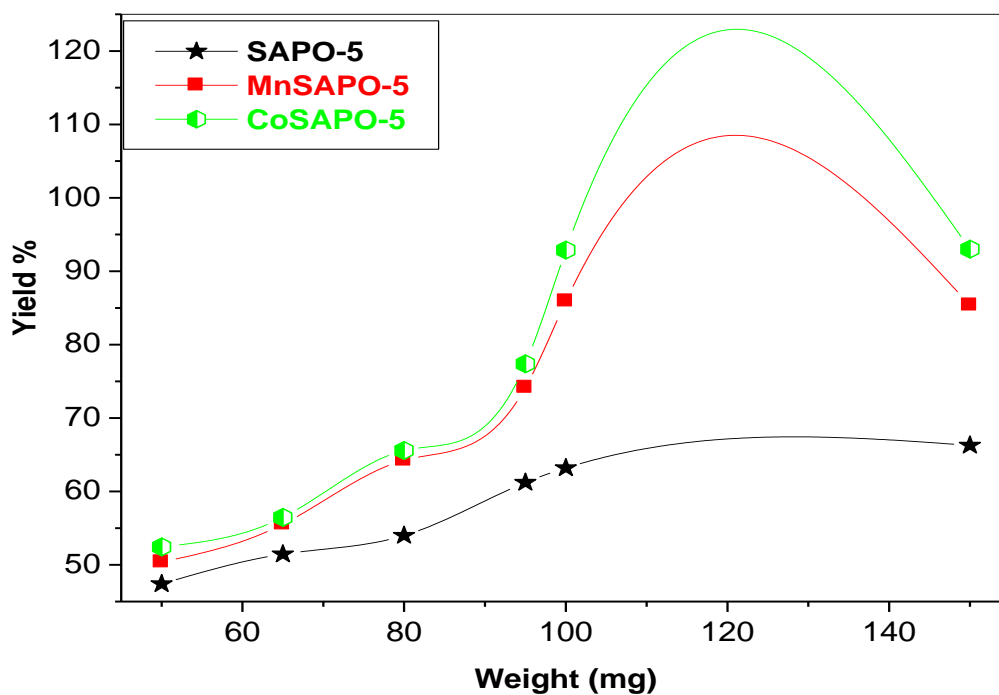


Graph 4.1.3.2(c). Effect of reaction time on the yield of butyl actate over various catalytic forms of SAPO-34

## 4.1.3.3 Effect of weight of catalyst

## 4.1.3.3(a). Effect of weight of catalyst on the yield of butyl acetate over various catalytic forms of SAPO-5

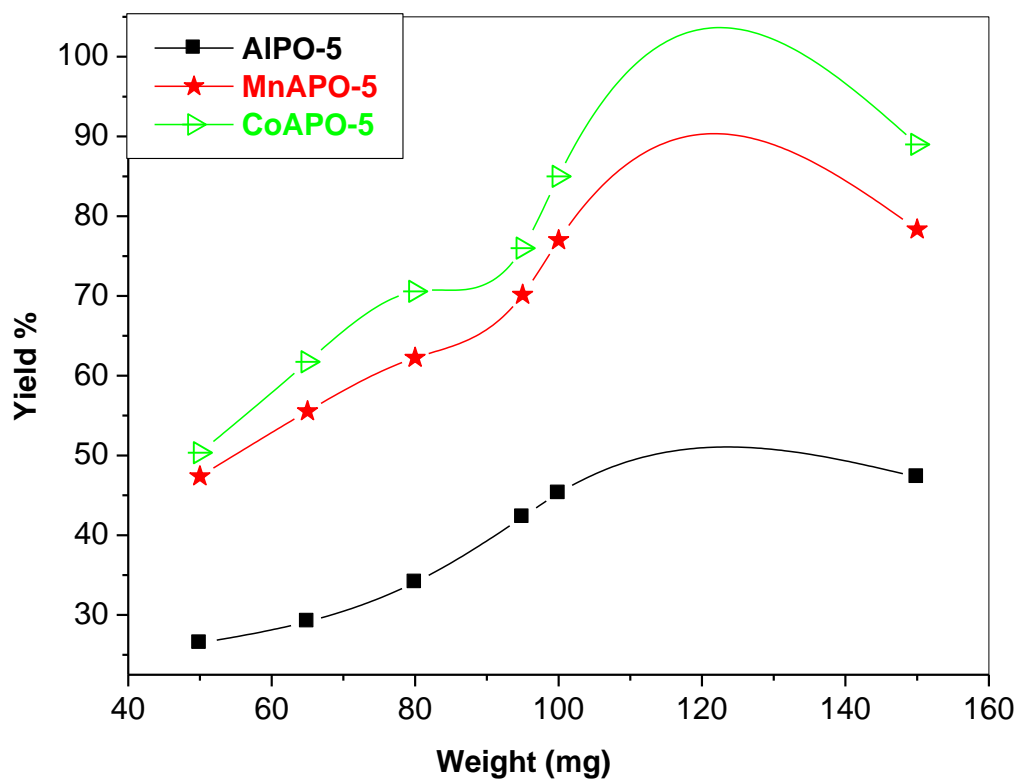
Weight (mg)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
50	47.41	50.38	52.44
65	51.47	55.54	56.47
80	54.00	64.25	65.58
95	61.22	74.15	77.38
100	63.21	85.91	92.88
150	66.28	85.35	93.01



Graph 4.1.3.3(a). Effect of weight of catalyst on the yield of butyl acetate over various catalytic forms of SAPO-5

Table 4.1.3.3(b). Effect of weight of catalyst on the yield of butyl acetate over various catalytic forms of AlPO-5

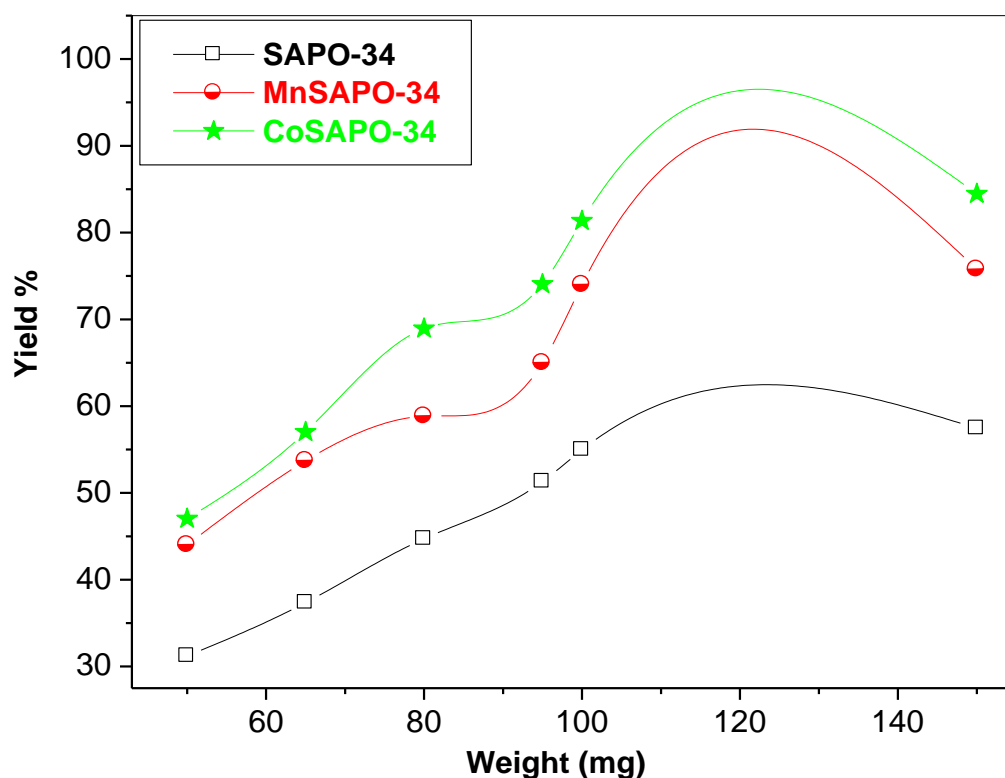
Weight (mg)	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
50	26.47	47.38	50.34
65	29.17	55.54	61.74
80	34.09	62.25	70.58
95	42.27	70.15	76.00
100	45.27	76.99	85.00
150	47.28	78.35	89.01



Graph 4.1.3.3(b). Effect of weight of catalyst on the yield of butyl acetate over various catalytic forms of AlPO-5

Table 4.1.3.3(c). Effect of weight of catalyst on the yield of butyl acetate over various catalytic forms of SAPO-34

Weight (mg)	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
50	31.22	44.02	47.04
65	37.36	53.71	57.02
80	44.72	58.85	68.95
95	51.31	65.00	74.07
100	54.97	74.00	81.36
150	57.45	75.77	84.47

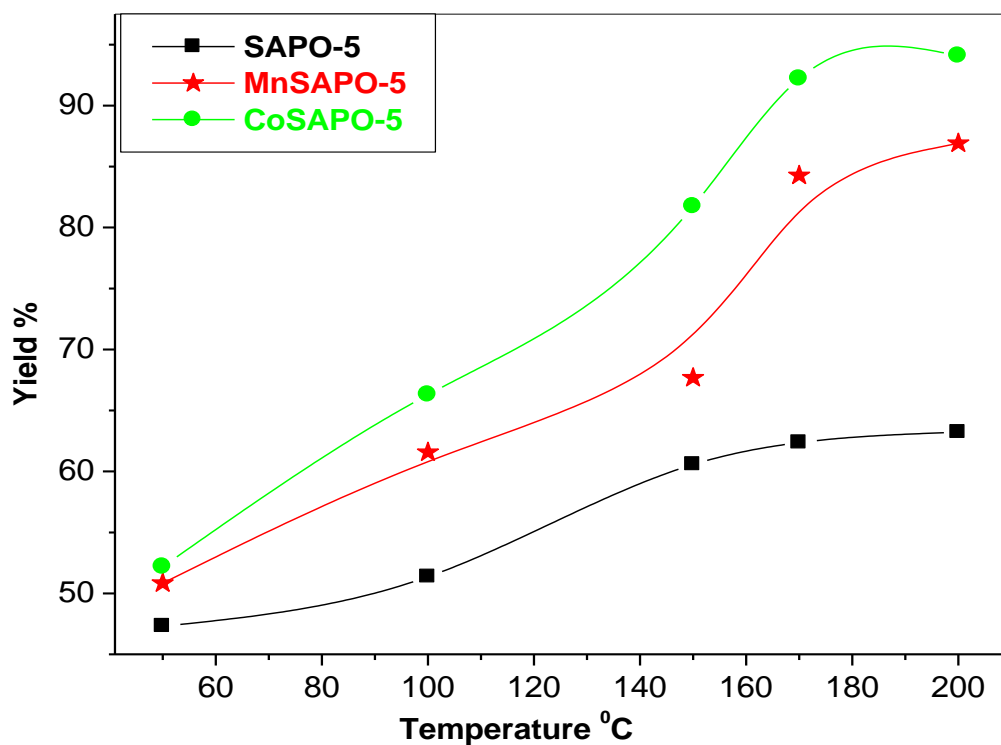


Graph 4.1.3.3(c). Effect of weight of catalyst on the yield of butyl acetate over various catalytic forms of SAPO-34

## 4.1.3.4 Effect of temperature

## 4.1.3.4(a). Effect of temperature of reaction on the yield of butyl acetate over various catalytic forms of SAPO-5

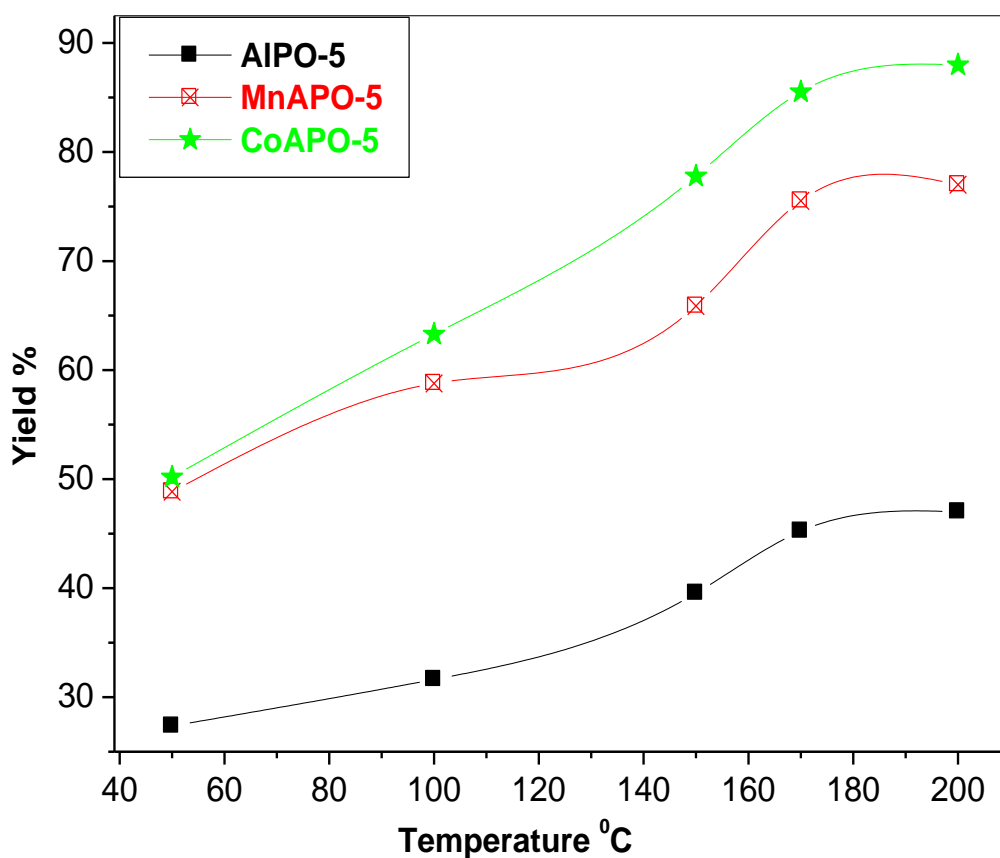
Temperature (°C)	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
50	47.31	50.84	52.18
100	51.36	61.57	66.29
150	60.57	67.68	81.74
170	62.36	84.27	92.20
200	63.21	86.91	94.08



Graph 4.1.3.4(a). Effect of temperature of reaction on the yield of butyl acetate over various catalytic forms of SAPO-5

Table 4.1.3.4(b). Effect of temperature of reaction on the yield of butyl acetate over various catalytic forms of AlPO-5

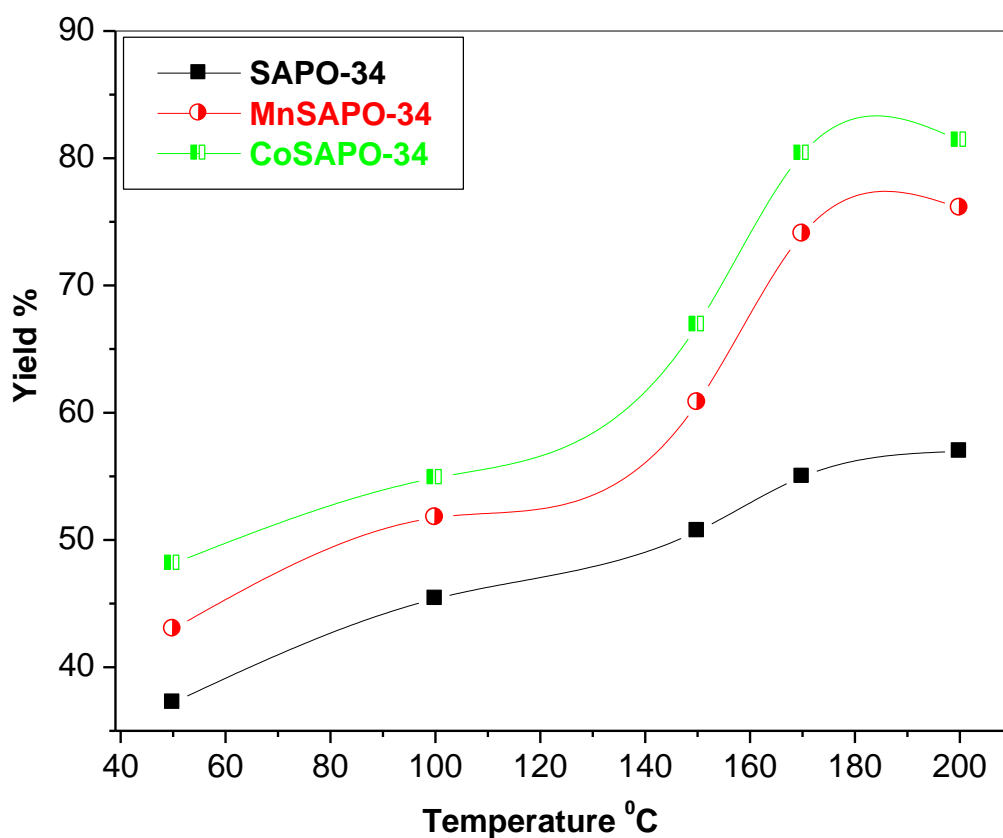
Temperature (°C)	% yield of catalytic forms		
	AlPO-5	MnAPO-5	CoAPO-5
50	27.36	48.84	50.18
100	31.63	58.77	63.29
150	39.54	65.88	77.79
170	45.24	75.52	85.52
200	47.00	77.01	87.99



Graph 4.1.3.4(b). Effect of temperature of reaction on the yield of butyl acetate over various catalytic forms of AlPO-5

Table 4.1.3.4(c). Effect of temperature of reaction on the yield of butyl acetate over various catalytic forms of SAPO-34

Temperature (°C)	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
50	37.22	43.00	48.14
100	45.38	51.75	54.88
150	50.70	60.80	66.90
170	54.97	74.04	80.36
200	56.97	76.08	81.39



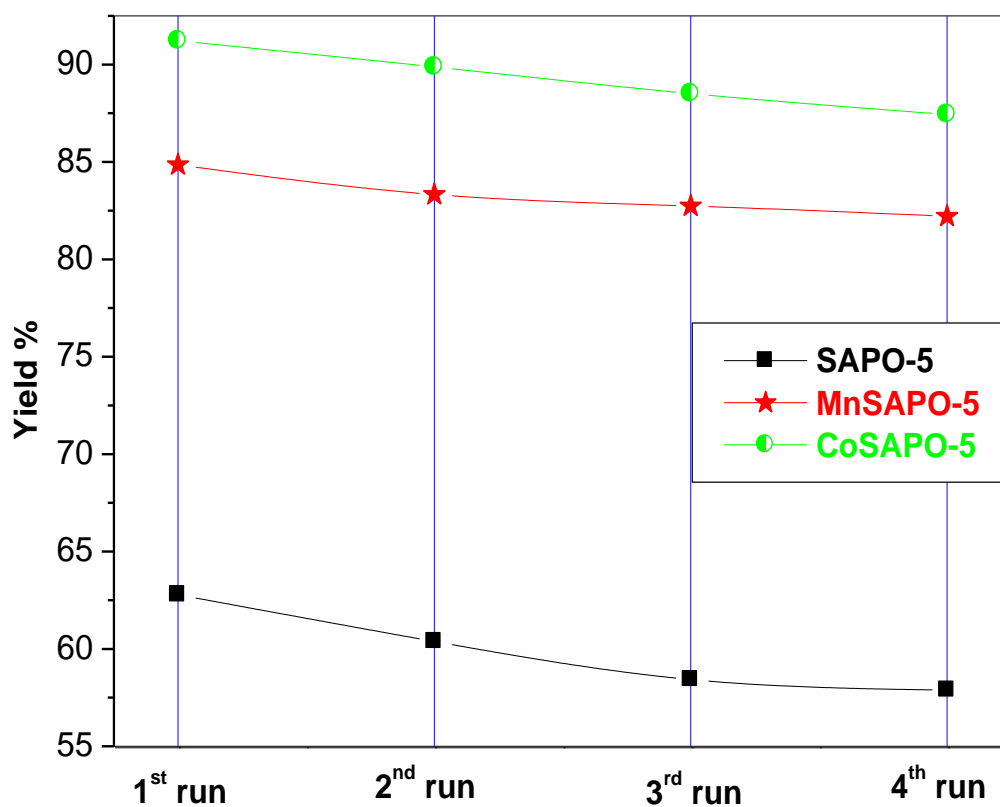
Graph 4.1.3.4(c). Effect of temperature of reaction on the yield of butyl acetate over various catalytic forms of SAPO-34



## 4.1.3.5 Effect of catalyst recycling

Table 4.1.3.5(a). Effect of catalyst recycling on the yield of butyl acetate over various catalytic forms SAPO-5

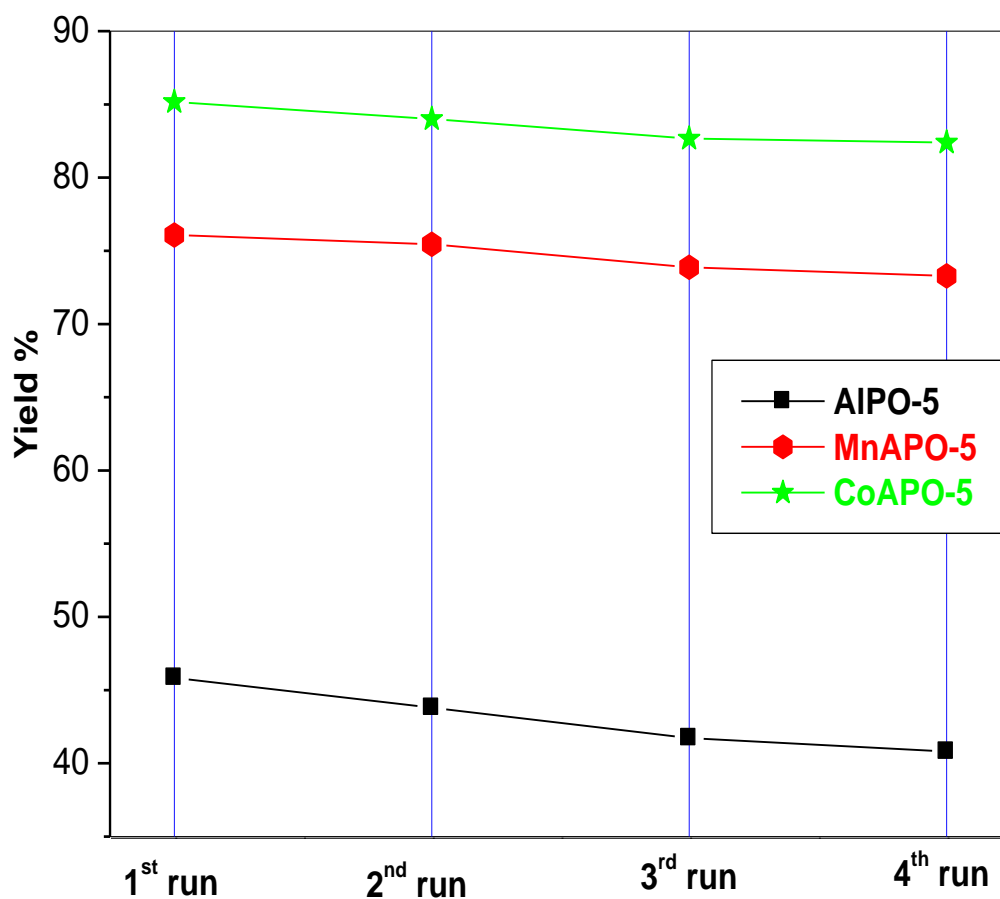
Runs	% yield of catalytic forms		
	SAPO-5	MnSAPO-5	CoSAPO-5
1 <sup>st</sup> run	62.78	84.85	91.22
2 <sup>nd</sup> run	60.38	83.33	89.88
3 <sup>rd</sup> run	58.43	82.74	88.51
4 <sup>th</sup> run	57.89	82.21	87.44



Graph 4.1.3.5(a). Effect of catalyst recycling on the yield of butyl acetate over various catalytic forms SAPO-5

Table 4.1.3.5(b). Effect of catalyst recycling on the yield of acetate over various catalytic forms AIPO-5

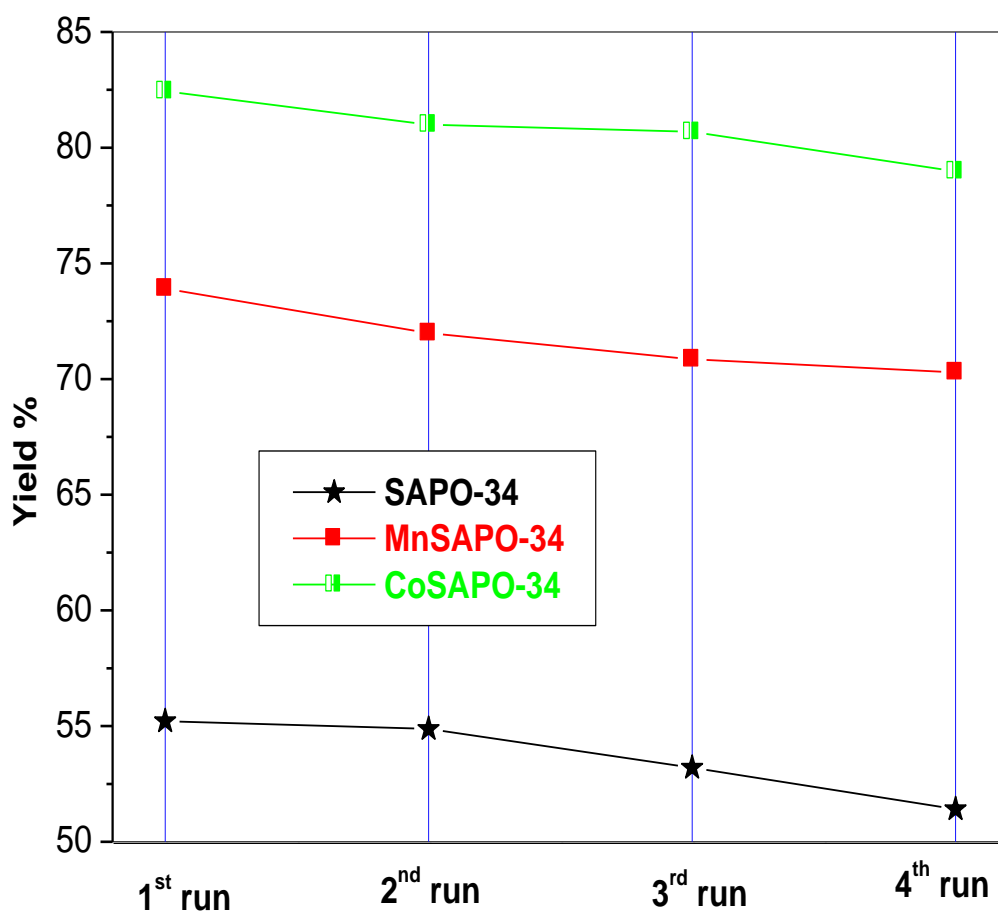
Runs	% yield of catalytic forms		
	AIPO-5	MnAPO-5	CoAPO-5
1 <sup>st</sup> run	45.84	76.08	85.17
2 <sup>nd</sup> run	43.80	75.45	84.00
3 <sup>rd</sup> run	41.72	73.88	82.67
4 <sup>th</sup> run	40.81	73.29	82.40



Graph 4.1.3.5(b). Effect of catalyst recycling on the yield of acetate over various catalytic forms of AIPO-5

Table 4.1.3.5(c). Effect of catalyst recycling on the yield of acetate over various catalytic forms SAPO-34.

Runs	% yield of catalytic forms		
	SAPO-34	MnSAPO-34	CoSAPO-34
1 <sup>st</sup> run	55.21	73.91	82.44
2 <sup>nd</sup> run	54.88	71.99	81.00
3 <sup>rd</sup> run	53.20	70.85	80.68
4 <sup>th</sup> run	51.41	70.29	78.98



Graph 4.1.3.5(c). Effect of catalyst recycling on the yield of acetate over various catalytic forms of SAPO-34

## 4.2 Discussion

All the catalysts and their metal substituted forms show good catalytic activity in all the reactions. Catalytic efficiency varies depending on the synthesis variable and characteristics of catalyst like size of pores etc. The mechanism of synthesis is also an important factor. The nonsubstituted zeotype catalysts show less catalytic effect. On isomorphous substitution of zeotypes by cobalt and manganese metals, catalytic efficiency increases sharply and produces maximum product yield. Nonsubstituted catalysts show minimum yield of the product. However in case of SAPO-34 and SAPO-5 (parent materials), there is comparable yield than the metal substituted forms of aluminophosphates like MeAPO-5, MeSAPO-5 and MeSAPO-34. The trend in the catalytic efficiency of all the metal substituted zeotypes is as follows: nonsubstituted > Mn<sup>2+</sup> substituted > Co<sup>2+</sup> substituted. Theoretically nonsubstituted material has no strong Brønsted acidic sites because their framework is electrically neutral. Thus there are no strong acidic centres in their framework responsible for solid acidity. Mn and Co are from the same row of periodic table. Cobalt is a smaller size element than manganese. Due to this fact, electro negativity of cobalt is more than manganese. Thus Brønsted acidic sites generated due to cobalt are stronger than manganese. Hence cobalt shows greater catalytic efficiency as it can lose its framework proton more easily behaving as a Brønsted catalyst. However, in case of manganese it is assumed that Lewis acidity is dominant. Cobalt also forms redox couple of divalent and trivalent cobalt ions in framework thus; it may also be a reason for this effect. However, possibility of these couples to be present in the framework of a zeotype is negligible due to Loewenstein's rule. Additionally cobalt is more stable in framework than manganese in their divalent coordination because they have 3d<sup>5</sup> and 3d<sup>3</sup> electronic configurations which lead to greater stability of cobalt in the framework comparatively. These all effects make a composite effect in favour of cobalt to be more active than manganese. Percent yield obtained for different catalytic materials is in the order of SAPO-5 > AIPO-5 > SAPO-34. To understand this series of catalytic efficiency, it is assumed that acidic sites generated due to metal substitution, would be contributing as catalytic centres in the zeotypes. The above fact is supported by the fact that AIPO-5 shows lower catalytic efficiency than SAPO-5 and SAPO-34, as its framework does not have any substituted metal ion and hence catalytic centres. Thus aluminophosphate AIPO-5 has lower acidity than SAPO-5 even both have same

framework building scheme. However, acidic sites generated due to the incorporation of silicon are mildly acidic than the acidic sites generated due to the metal (cobalt and manganese) substitution. But, as the molar composition of silicon (0.03) in the synthesis recipes of silicoaluminophosphate is too much high as compare to the metal molar ratio (0.01), the number of acidic sites generated due to the silicon will be more and hence greater catalytic efficiency. In case of SAPO-34, effect of pore size is dominant than strength of acidic sites. Pore size of this material is  $2/3$  than that of AIPO-5. Additionally the structure of pores and channels of SAPO-34 is like a “bottle neck”. Both these facts exert an effect on reactants that is known as *effect of confinement* which checks larger molecules and does not allow entering them inside. Thus reaction occurs only at the surface of catalyst mostly, which in turn is responsible for the low yield of product over SAPO-34. Surface area is an important factor in catalysis but due to confinement effect, molecules of larger size than pore size of catalyst cannot penetrate inside the catalyst. Thus total surface area available to the reactants will be smaller leading to low yield. However in case of esterification reaction, all the reactants are small in size, thus catalytic efficiency of SAPO-34 even after its small pore size, is compatible with the other two catalysts. This fact is also in support of above consideration. In case of AIPO-5 and SAPO-34, there is no much difference in catalytic efficiency. Hence, it can be concluded that cobalt and manganese ions generate strong acidic sites in the framework than the mildly acidic sites generated due to silicon. Although SAPO-34 is having smaller pore size, its catalytic efficiency is comparable to those of other zeotypes having bigger sized pore which is due to larger surface area of SAPO-34. Thus total effect is that, SAPO-34 has about similar but lesser catalytic efficiency than AIPO-5. Another fact may be that AIPO-5 is more hygroscopic than SAPO-34 due to presence of two different atoms (Al & P), whose electro negativities are much more different than Si and Al in case of SAPO-34. Due to hygroscopic nature of AIPO-5, it may be adsorbing water and solvent molecules more than SAPO-34 which is less hygroscopic in nature. This is the reason behind lower yield of product shown by AIPO-5 than SAPO-34. To avoid this effect, all the solvents should be dried well before starting the reaction and selection of solvents should be done carefully. In support of this speculation, example of reaction carried out in water as a solvent can be taken where catalyst materials shows lower yield in water medium than the reactions in which other solvents were used.

Surface area of a catalyst plays important role in catalysis. But in case of this study, it is not a dominant factor than pore size. The results show that catalysts having greater surface area are more efficient. Thus surface area also plays a role in the determination of catalytic efficiency. In the synthesis of Imidazole, the efficiency of corresponding catalysts was found to be lower than in the synthesis of Quinoxaline and butyl acetate.

It is clear from mechanism of Imidazole that why the yield of this product is lower in comparison to other reactions. As in this reaction, two protons are required from catalyst to attach the reactant at a time to proceed the reaction. To understand its effect, crystallographic imagination is required which can make it clear. In all the aluminophosphate materials, molar percentage of metals (which generate acidic protons) is 0.01 %. Thus there is a minimum possibility for a framework composition to be having two protons at an adjacent position. Because, two neighbouring protons will be too much far which are required in this mechanism to attach at two adjacent oxygen of aldehyde reactant. Thus there will a need of extra collision to get the second proton from catalyst's surface which requires some more activation energy hence a lower product yield. In case of Quinoxaline synthesis, the size of reactants is comparatively lower than Imidazole. Thus more catalytic sites are accessed by reactants in case of Quinoxaline. Same reason is assumed in case of esterification reaction because reactants are too much smaller in comparison to the other two reactions.

Two reasons are there responsible for the catalytic activity of a zeotype. First one is the presence of framework defects which are assumed to be causing weak acidity. Second one is the presence of a substituted metal atom in the framework of zeotype which is responsible for Brønsted acidity. In my study, it was observed that AIPO-5 is the least efficient catalytically. Reason for its lowest efficiency is the absence of both the defect centres and Brønsted acid centres in AIPO-5. Thus in absence of both these sites, it is naturally catalytically inactive or less active. Calcination of AIPO-5 may cause fewer framework defects. Thus, whatever catalytic activity is shown by AIPO-5 may be due to presence of these defects.

The results obtained, in this study, for catalytic efficiency of SAPO-5 and SAPO-34 show that these catalysts have greater catalytic efficiency than AIPO-5 material. Presence of the acidic sites, generated due to the silicon atom are responsible

for this because silicon acts as a substituted metal ion and hence responsible to the Brønsted acid sites leading to greater efficiency of SAPO-5 and SAPO-34 than AIPO-5. However, amount of silicon incorporation in the framework is of limited nature to be incorporated. Thus, metal substituted forms of all these catalysts (MeSAPO-5, MeSAPO-34 and MeAIPO-5) show greater efficiency than these nonsubstituted catalytic forms or parent zeotypes (SAPO-5, SAPO-34 and AIPO-5).

Effect of recycling of catalyst materials was also examined and it was found that these catalysts are more suitable than other solid supported catalysts because in solid supported catalysts, problem of catalytic sites' leaching is a main problem. Catalysts used in this study show constant catalytic activity on recycling and their catalytic sites do not get leached as these sites are framework (chemically bonded) sites. Thus, it is confirmed that catalytic centres are stable in these zeotype catalysts. Hence, use of these catalysts is sustainable and can be utilised as green solid acid catalyst after few modifications.

Effect of solvent is unpredictable as water (as a solvent) shows lower catalytic activity. Reason was interpreted that adsorption of the water molecules on catalytic sites led to lower catalytic efficiency of a catalyst in water medium. Thus attempts should be made to synthesize less polar framework and defect less framework. The use of conventional liquid acid catalysts can be replaced totally if incorporation of metal atoms in the framework these zeotypes is increased upto unity. However, practically to achieve this framework composition it is not a straight one. These solid acid catalysts may solve the various environmental problems highlighted in the first chapter due to these properties.

- ❖ Recycling of these catalysts is possible with minimum changes in their efficiency.
- ❖ Synthesis is simple and no hazardous reagent release.
- ❖ Acidity is regulable and depends on the metal amount incorporated in the framework.
- ❖ Shape selectivity of these catalysts makes them more valuable than conventional catalysts.
- ❖ Disposal of these catalysts is not an environmental issue.