



AMINATION OF ALCOHOLS CATALYSED BY MOLYBDENUM SPECIES PROMOTED HYDRATED ALUMINA

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Abstract

Al(OH)₃, Zr(OH)₄ and MgO supports were impregnated with ammonium heptamolybdate by incipient wetness to obtain 5 wt % Mo containing supports. Materials thus prepared were characterized through % composition of Mo, surface area, X-ray diffraction pattern, and FTIR spectroscopy. Catalytic activity measurements were carried out in amination of benzyl alcohol. N-benzyl aniline (NBA) was the major product formed when aniline was used for amination of benzyl alcohol. NBA was formed only over Mo/Al(OH)₃ and Mo/Zr(OH)₄, but not over Mo/MgO catalysts. NBA is formed with higher yield over Mo/Al(OH)₃ catalyst. The influence of change in molar ratio of the reactants, duration of the reaction, weight of the catalyst and the effect of solvents have been determined using Mo/Al(OH)₃ catalyst over the reaction between benzyl alcohol and aniline. In addition, amination of benzyl alcohol using aliphatic, cyclic and side chain substituted amines over Mo/Al(OH)₃ are also reported in this paper.

Key words: Mo/Al(OH)₃, Mo/Zr(OH)₄, amination of benzyl alcohol, N-benzyl aniline

1. INTRODUCTION

Amines have practical importance in fine chemical synthesis, finding use as antioxidants in fuel oils, rubber stabilizers, medicinal drugs, detergents, herbicides, dyes, organic materials with important electronic properties and ligands for transition metals [1, 2]. Generally an alcohol is first converted to a halide to form an amine. Some of the catalysts reported for the direct conversion of alcohols into amines are Ph₃P⁺ N MeC₆H₄I/Buⁿ NH Me/ DMF [3], Al(OBu^t)₃/RaneyNi [4], CuO/Cr₂O₃/Na₂O/SiO₂/H₂O [1], CuO/Al₂O₃ [5], RuCl₂(PPh₃)₂/Ph₃P [6] and methylrhenium trioxide [7]. Amination of aromatic bromides mediated on the surface of KF-alumina and palladium are also

reported recently [2]. In this paper we report a direct conversion of a primary amine to a secondary amine over molybdenum oxo-species promoted aluminum hydroxide via amination of benzyl alcohol.

Supported Mo catalysts are generally used in partial oxidation of alcohols and olefins [8-14] metathesis [15], ethylene polymerization and hydrodesulphurization [16, 17]. Recently, we have reported that Mo (5%)/Al(OH)₃ brings about dehydration of benzyl alcohol to yield dibenzyl ether and higher % wt of molybdenum does not catalyze dehydration reaction instead it catalyses disproportionation reactions [18, 19, 20]. This has prompted us to try the dehydration reaction between two unlike molecules such as benzyl alcohol and aniline. When these two different substrates were used in the study we made an interesting observation which has been reported in detail in this paper. Further, apart from Al(OH)₃ support other supports such as Zr(OH)₄ and MgO are also chosen to study the effect of Mo oxo-species on these supports and their application in amination reaction.

Further, amination reaction is conducted using various alcohols and amines. Since reaction between benzyl alcohol and aniline was giving better yield of product over Mo/ Al(OH)₃ catalyst, a detailed work on the effect of molar ratio of the reactants, weight of the catalyst, solvents and duration of the reaction were conducted systematically on this reaction.

2. Experimental

2.1. Preparation of the catalysts.

Aluminum hydroxide is prepared by the hydrolysis of aluminum isopropoxide and dried at 120 °C. MgO is obtained by the calcination of MgCO₃ at 350 °C. Zirconium hydroxide sample is obtained commercially (aldrich) and dried at 120 °C overnight. All the three supports were subjected to incipient wetness impregnation using aqueous solution containing requisite amount of ammonium heptamolybdate to obtain finally 5 wt % molybdenum in the samples. After impregnation all the samples were dried initially at 120 °C overnight and finally suffered calcination at 550 °C for 5 hours. It is to be noted here that since aluminum hydroxide and zirconium hydroxide are not calcined to 550 °C prior to impregnation, the catalysts obtained from them will be represented as zirconium hydroxide and aluminium hydroxide/hydrated alumina supported catalysts. However all comparisons of physicochemical properties between the supports and Mo/ support samples have been carried out after final calcinations at 550 °C, hence pure support may be called for convenience as alumina and zirconia.

2.2. Characterization of the catalysts.

For the determination of Mo content in the catalyst samples, a known amount of each catalyst was

dissolved in a suitable acid. Hot Conc. H_2SO_4 , a mixture of Conc. $\text{H}_2\text{SO}_4 - \text{HClO}_4$ and Conc. HCl were used as solvents for the complete dissolution of $\text{Mo}/\text{Al}(\text{OH})_3$, $\text{Mo}/\text{Zr}(\text{OH})_4$ and Mo/MgO catalysts respectively. On treating these solutions with SnCl_2 solution and thiocyanate ion, a red color complex $\text{Mo}(\text{SCN})_5$ is formed which has maximum absorption at 465 m μ . The concentration of Mo in the solutions was estimated calorimetrically. Detailed procedure is given elsewhere [21]. (Note: Absorbance should be recorded within a few hours. On prolonging color changes to orange red, leading to erratic reading).

Surface area of the supports and supports containing molybdenum was measured by N_2 adsorption at 77 K by the BET method using a NOVA-1000 (VER: 3.7) instrument. To check the crystallographic phases present in the samples powder X-ray diffraction patterns were recorded using a Philip's X'pert Pro diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) using graphite monochromator to filter the $\text{K}\beta$ lines. PXRD was collected at a scan rate of 2 $^\circ$ /minute with a 0.02 $^\circ$ step size for 2θ from 10 $^\circ$ to 60 $^\circ$. IR absorption spectra of all the supports and supports containing molybdenum species were recorded by the KBr pellet method over the range 4000-400 cm^{-1} using a Jasco FTIR-410 instrument, to get information about hydroxyl groups and nature of molybdenum oxo species.

2.3. Catalytic activity study.

All the catalytic activity measurements were carried out in liquid phase. To begin with benzyl alcohol and aniline were taken in the molar ratio 1:1 (keeping the total volume 10 ml) in a R.B flask fitted with a water condenser and refluxed with 0.5 g of the catalyst for 6h. The solid catalyst was separated by filtration and thin layer chromatographic analysis of products indicated the presence of three components. Further, quantitative analyses of product mixture were carried out using GC containing 10% SE 30 chromosorb column. The major product was separated using silica column and eluted with ethyl acetate and n-hexane in the ratio 1:19 and further characterized by ^{13}C NMR, ^1H NMR, IR and LRMS. Furthermore studies were conducted meticulously by changing the molar ratio, amount of the catalyst, duration of the reaction and the solvents.

In order to check the activity of $\text{Mo}/\text{Al}(\text{OH})_3$ catalyst in the amination of benzyl alcohol, reactions were conducted using aromatic side chain substituted, cyclic and aliphatic amines and the results have been reported here.

3. RESULTS AND DISCUSSION.

3.1. Percentage composition of molybdenum

The % wt of molybdenum present in all the three catalysts are given in table 1. Since the catalyst was

completely dissolved in a suitable solvent estimation of molybdenum by this method gives exact amount of molybdenum present in the sample.

3.2. Surface area

Specific surface area of pure supports and those containing 5 wt % Mo are given in Table 1. Surface area of pure $\text{Al}(\text{OH})_3$ and MgO supports increased on calcination to $550\text{ }^\circ\text{C}$ whereas that of $\text{Zr}(\text{OH})_4$ decreased. Among all the three supports, surface area of alumina was more than the other two supports after calcination. Reduction in surface area was observed on incorporation of molybdenum into the support except in the case of zirconia. The decrease in surface area can be attributed to the penetration of molybdenum species into the pores of the support [22]. The increase in surface area of $\text{Zr}(\text{OH})_4$ support in the presence of Mo indicates that, Mo species prevent sintering of the support during calcination to some extent.

3.3. X-ray diffraction

XRD patterns of pure supports are given elsewhere [18,19]. X-ray diffraction patterns of all the supports containing 5 wt% molybdenum are shown in figure 1. None of the samples exhibited diffraction peaks characteristic of crystalline MoO_3 . $\text{Mo}/\text{Al}(\text{OH})_3$ sample was X-ray amorphous in nature whereas $\text{Mo}/\text{Zr}(\text{OH})_4$ and Mo/MgO were crystalline in nature. $\text{Mo}/\text{Zr}(\text{OH})_4$ sample exhibited peaks characteristic of monoclinic and tetragonal phases of zirconia. The tetragonal phase was more prominent compared to monoclinic phase. The decrease in the intensity of monoclinic phase of $\text{Mo}/\text{Zr}(\text{OH})_4$ compared to the monoclinic phase of pure zirconia, indicates that presence of molybdenum species destroy monoclinic phase of zirconia to certain extent [23, 24]. Neither $\text{Zr}(\text{MoO}_4)_2$ nor crystalline MoO_3 are formed on this sample. This clearly indicates that molybdenum species are well dispersed on zirconium hydroxide support.

As far as the Mo/MgO sample is concerned, peak at 2θ value 42.7 corresponds to MgO (JCPDS 01-1235) and the one at 28.7 corresponds to $\alpha\text{-MgMoO}_4$ (JCPDS 31-0796). Thus during impregnation and subsequent calcination basic MgO would have reacted with acidic precursor ammonium heptamolybdate to form crystalline MgMoO_4 .

Among the three different supports containing Mo catalyst only $\text{Mo}/\text{Al}(\text{OH})_3$ was amorphous in nature and the presence of molybdenum species on this support did not cause any phase transition like in the case of supports of the other two. This kind of difference in metal species interaction with the support which resulted in well dispersed molybdenum species on aluminum hydroxide may be attributed to its enhanced catalytic activity in presence of molybdenum species, as described later in

this paper.

Decrease in the surface area value of the molybdenum containing supports and the absence of crystallites of MoO₃ indicate that the molybdenum species are well dispersed on the surface of supports on account of its interaction with the supports including even in the narrow pores.

3.4. FTIR

FTIR patterns of supported Mo catalysts are shown in Figure 2. Since there was an overlapping of absorption region of Al-O and Mo-O stretching bands, it was unable to distinguish between these two [25]. From the spectrum of Mo/Al(OH)₃, the spectrum of pure support was subtracted to obtain more information about the kind of Mo oxospecies. A broad band at 926 cm⁻¹ is observed in the Mo=O vibrational stretching region. This is assumed to be due to surface bound Mo species, probably octahedral (Oh) polymolybdate or isolated tetrahedral species. The band of Mo-O-Mo species in the lower wave number region (767 cm⁻¹) indicates octahedral Mo (Mo_{Oh}). The band at 926 cm⁻¹ is not observed for crystalline MoO₃; thus this is due to surface bound species [26]. According to previous data [21, 22], the weak band in the range 970-930 cm⁻¹ is assigned to the terminal Mo=O stretching of the hydrated form of the surface molybdenyl species like [O₃M=O]²⁻. In line with XRD patterns, no evidence of bulk MoO₃ bands near 960 cm⁻¹ with complex overtones at 1955, 1925 and 1833 cm⁻¹ are found [27].

In the case of Mo/Zr(OH)₄ sample the band at 968 cm⁻¹ is assigned to the terminal Mo=O stretching of the hydrated form of the surface molybdenyl species. Mo/MgO sample exhibited bands at 855 cm⁻¹ and 1018 cm⁻¹ which are characteristic of MoO₄²⁻ [28-30]. Hence FTIR results are in agreement with XRD patterns.

3.5. Catalytic activity studies

Amination of benzyl alcohol using aniline over all the three pure supports and Mo/ support were interesting, as the % conversion of aniline to NBA varied significantly over the different catalysts ranging from zero to 100. Among pure supports, only alumina was active towards amination reaction, as it converted 61 % of aniline to N-benzyl aniline, while MgO and ZrO₂ supports were inactive towards the aforesaid reaction (Table 2). This indicates that the active sites responsible for this reaction is absent in MgO and ZrO₂ and present in alumina support.

Interestingly, the trend was different when these supports were incorporated with 5 wt % molybdenum. The basic support MgO which failed to show any activity in the pure form continued to be so even in the presence of molybdenum. However Mo/ Zr(OH)₄ could convert 59 % of aniline to

secondary amine. This tendency in the catalytic activity may be attributed to the kind of molybdenum species that is present on different types of supports as well as metal oxo species-support interaction. As is clear from PXRD that well dispersed molybdenum species are formed over aluminum hydroxide and zirconium hydroxide supports. Whereas no such kind of dispersion occurred on MgO support instead MgMoO_4 compound was formed. This compound which is crystalline in nature is seems to be inactive for the amination of alcohol. On the contrary, well dispersed molybdate species on aluminum hydroxide and zirconium hydroxide are capable of carry out amination of benzyl alcohol. Absence of NBA formation over pure zirconia and the formation of this product over zirconium hydroxide supported molybdenum species indicate that pure zirconia has only the role of an inert support and it is the well dispersed molybdenum species that is responsible for the amination reaction. Instead of zirconium hydroxide when aluminum hydroxide is taken as the support both support as well as the well dispersed molybdenum species concurrently brought out intermolecular dehydration. It is this cumulative effect of the support as well as the molybdenum species which contributed to the high yield of NBA in the case of Mo/ $\text{Al}(\text{OH})_3$. Since aniline is converted only to NBA whereas benzyl alcohol is also converted to dibenzyl ether (DBE) over Al_2O_3 , Mo/ $\text{Al}(\text{OH})_3$, ZrO_2 , Mo/ $\text{Zr}(\text{OH})_4$ due to the dehydration of benzyl alcohol, % yield of NBA is expressed in terms of % conversion of aniline. % formation of DBE was less than 10. Formation of DBE can be attributed to acid sites present on these samples [31]. The lower % of DBE shows that, the dehydration reaction between benzyl alcohol and aniline is preferred over dehydration between two benzyl alcohol molecules. This is because between aniline and benzyl alcohol, aniline being more basic in nature gets adsorbed on acid sites of the catalyst which in turn reduces the activation energy required for the reaction between benzyl alcohol and aniline. Absence of disubstituted product of aniline can be attributed to the presence of bulkier- $\text{CH}_2\text{C}_6\text{H}_5$ group on nitrogen of aniline.

The preliminary studies on pure alumina support and aluminum hydroxide containing molybdenum species indicated two aspects. Firstly, alumina is capable of carry out intermolecular dehydration between aniline and benzyl alcohol and secondly, this property of alumina is enhanced on the addition of small amount of molybdenum species (5 wt% Mo). Pyridine adsorption studies of these two samples indicated the presence of Lewis acid sites. Hence it may be inferred that dehydration between aniline and benzyl alcohol takes place over Lewis acid sites.

This kind of promotive effect of molybdenum species is exploited here in the preparation of secondary amine from primary amine. Since Mo/ $\text{Al}(\text{OH})_3$ was catalytically more active compared to other catalysts. Further studies on the amination of benzyl alcohol using aniline over Mo/ $\text{Al}(\text{OH})_3$

were carried out to optimize the reaction conditions to get better yield and the results are discussed below.

Effect of molar ratio

Amination reaction over Mo/ Al(OH)₃ was found to be stoichiometrically good as the % yield of N-benzyl aniline was 80 with 1:1 molar ratio of benzyl alcohol and aniline. However on increasing the molar ratio of benzyl alcohol to aniline, a complete conversion of aniline to NBA was possible at 4:1(Benzyl alcohol: aniline). Table 3

Effect of reaction time

The reaction between benzyl alcohol and aniline was carried out at 2, 4, 6, 8, 12 and 14 hours durations. % conversion increased noticeably from 4 h to 8h and remained almost constant upto 12 hrs (figure 3). Hence 6 hrs seems to be optimum time for this reaction and further optimization reactions were conducted for 6 h duration.

Effect of weight of the catalyst.

The success of any catalyst not only depends on its ability to give better yield but also on the usage of catalytic amount. To see the application of Mo/ Al(OH)₃ as a good catalyst, the amount of catalyst was varied (0.2, 0.5, 1 and 1.5g), keeping other parameters (molar ratio; 1:1, duration ; 6 hrs) constant. From figure 5 it is clear that even as small as 0.2g of the catalyst can convert aniline to N-benzyl aniline to an extent of 73 %. However, there was increase in the % conversion of aniline with increase in the amount of the catalyst (Figure 4). An increase in the amount of catalyst from 0.2 g to 1.5 g resulted in 20 % increase in the % conversion of aniline to NBA .

Effect of presence of solvent

Many organic reactions yield product better in the presence of a suitable solvent. Though a significant N-benzyl aniline % was formed even in the absence of any solvent, reactions were carried out in the presence of various low and high boiling solvents which are either polar or nonpolar. Methanol, toluene, dry benzene, chloroform, acetone and Tetrachloroethane (TCE) were the solvents used for these studies. Surprisingly no NBA was formed in the presence of any of these solvents, except in the case of TCE (80 %). Had, polarity of the solvent a criterion for the conversion of aniline, product would have been formed over other polar solvents like alcohols also. Absence of any product in the presence of all other polar and nonpolar solvents indicates that polarity of the solvent is an irrelevant factor here. Boiling point of the solvent is another factor to be looked into. When the reaction mixture is heated in the presence of a solvent refluxing was taking place at a temperature of the lowest boiling

point constituent (~170 °C; noted to be the temperature of refluxing mixture). The common factor for all other solvents except tetrachloroethane is that their boiling points are low compared to TCE. Hence it can be inferred that in the presence of low boiling point solvents amination of benzyl alcohol doesn't proceed. Hence heating at high temperature is essential for the reaction to proceed in the required direction. It is noteworthy that the yield is equally good in the absence of a solvent as well as in the presence of TCE. Hence amination of benzyl alcohol can be carried out in the absence of any solvent, which is an added advantage of this catalyst.

Reusability of the catalyst.

To affirm the usability of Mo/Al(OH)₃ catalyst as a new catalyst in the amination of benzyl alcohol the catalyst was recycled thrice. It was found that this particular catalyst can be recycled with out much reduction in the activity. The yield was between 79 and 80% in all the three trials.

Amination of benzyl alcohol using other amines.

Amination of benzyl alcohol using other amines such as benzyl amine, cyclohexyl amine and n-propyl amine resulted in different % conversion of amines. The results are given in table 4.

In the amination reaction using different amines, the % conversion of aniline was maximum (80%) followed by benzyl aniline and cyclohexyl amine and the conversion was least with n-propyl amine. This result indicate that Mo/Al(OH)₃ catalyst is specific for aromatic amines and less or least active with cyclic or aliphatic amines.

The difference in the conversion of amines can be explained as follows. The lone pair of electron on nitrogen gets delocalized to the benzene ring of aniline making the ortho/para position electron rich. Electron rich para position gets attached to Lewis acid sites [32]. It is known that incorporation of molybdena on alumina increases the Lewis acid sites [33]. Delocalization of electron is less in the case of benzyl amine resulting in reduction of adsorption on the acid sites and hence less % conversion. The reduction in the % conversion of cyclo hexyl amine and n-propyl amine can also be related to lack of delocalization of electron in these molecules.

CONCLUSIONS

Amination of benzyl alcohol can be carried out over alumina, molybdena promoted aluminum hydroxide and zirconium hydroxide. However the conversion is maximum with molybdenum species promoted aluminum hydroxide. The present method offers considerable advantages in terms of simplicity, high chemoselectivity, high atom efficiency, low environmental impact and one of the most cost- effective processes. Hence it can be concluded that molybdena promoted aluminum hydroxide

catalyst satisfies all the conditions required for a good heterogeneous catalyst.

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Table 1: Physico- Chemical Properties of Catalysts and Molybdenum Promoted Catalysts.

Catalyst	Specific surface area m ² /g	% composition of molybdenum
Al	168(211)	-
AlMo -5	205	4.9
ZrO ₂	176(32)	-
ZrOMo-5	42.3	4.9
MgO	43(178)	-
MgOMo- 5	109.8	5.1

Al: Aluminum hydroxide support. Surface area of calcined supports are

given in the parenthesis

AlMo -5 : Aluminum hydroxide support containing 5 wt% molybdenum.

Table 2: % Conversion Of Aniline And % Selectivity Of N- Benzyl Aniline During Amination Of Benzyl Alcohol.

Support/catalyst	% conversion of aniline	% selectivity for N-benzyl aniline
Al	61	80
AlMo -5	80.2	86
ZrO ₂	0.0	0.0
ZrO Mo-5	59	59
MgO	0.0	0.0
MgO Mo- 5	0.0	0.0

Dibenzyl ether was another product (yield less than 10%). Unidentified product < 5%.

Al: calcined aluminum hydroxide support. AlMo -5: aluminum hydroxide containing 5 wt % molybdenum. Weight of the catalyst 0.5g ; reaction time: 6 h.

Table 3: Unidentified Products 5%

Molar ratio(OH:NH ₂)	% conversion of aniline
1:1	80
2:1	80
3:1	81
4:1	100

Table 4: % conversion of different amines in the reaction with benzyl alcohol

Amines	% conversion
Aniline	80.2
Benzyl amine	53.7
Cyclohexyl amine	20.4
n-propyl amine	7.0

Molar ratio of Benzyl alcohol: amine 1:1. Duration of reaction 6 h.

Figure captions

Figure1: Powder X-ray diffraction patterns of 5 wt % molybdenum containing supports.

Figure 2 : FTIR of a) AlMo 5, b) ZrMo 5 and c) MgMo 5

Figure 3. Amination of benzyl alcohol using aniline. Effect of reaction time.

Figure 4: Amination of benzyl alcohol using aniline. Effect of amount of molybdenum species

promoted aluminum hydroxide catalyst.

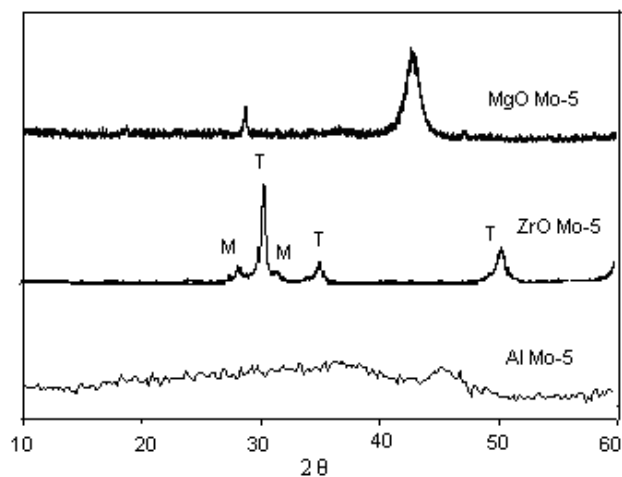


Figure 1

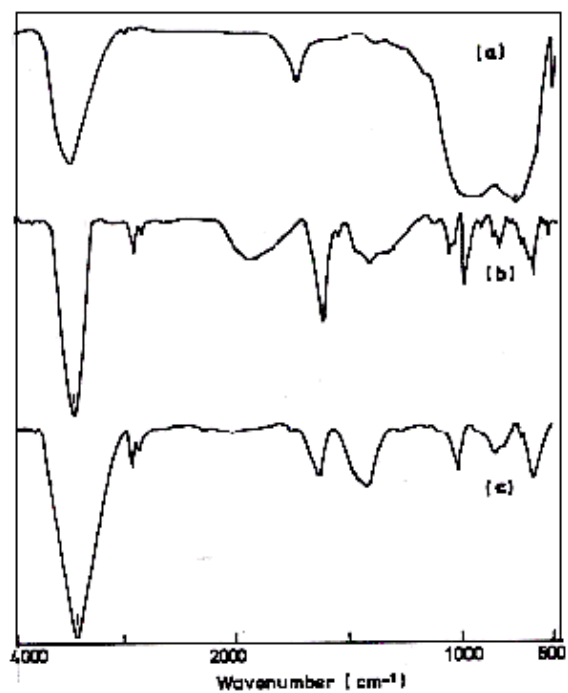


Figure 2: AlMo 5, b) ZrMo 5 and c) MgMo 5

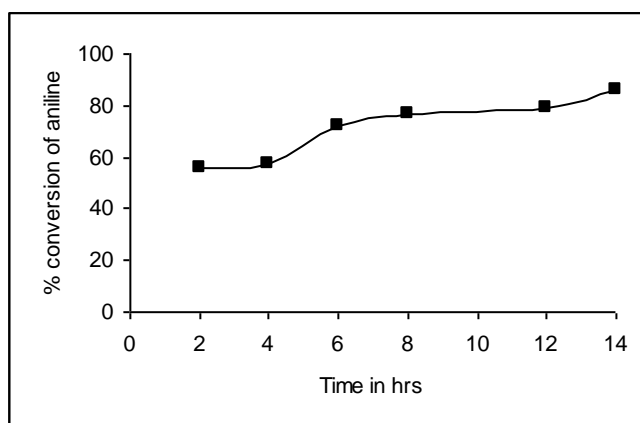


Figure 3:

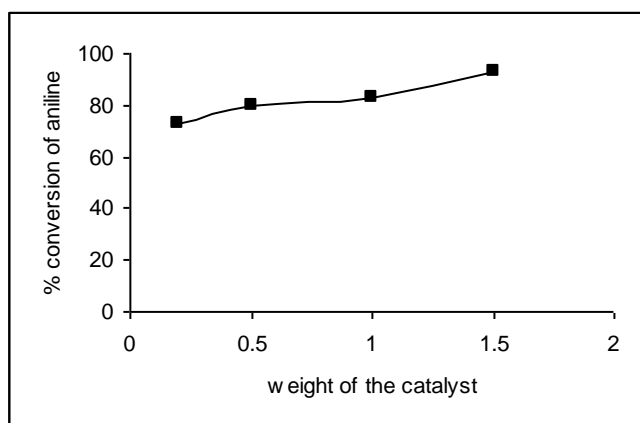


Figure 4