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Synthesis of Acetamide Derivatives using S-MWCNT and S-MC as an Efficient Heterogeneous Catalysts

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Sulphate modified multiwalled carbon nanotubes (S-MWCNT) and Mesoporous carbon (S-MC) catalysts were prepared by wet impregnation method. These materials were characterized by different analytical techniques such as Powder-XRD, BET surface area analysis, SEM–EDS and TEM analysis to evaluate their bulk and surface properties. Surface acidity of the catalyst was measured by TPD-NH_3 technique, as well as *n*-butyl amine titration. The estimated surface acidity of S-MWCNT and S-MC using *n*-butyl amine titration was found to be 0.82 and 1.75 mmol/g respectively. The catalytic activity of these materials was investigated in the synthesis of acetamide derivatives using aromatic acids with substituted aromatic amines in a liquid phase reaction. The reaction conditions were optimized to achieve good % yield of the products. In general S-MC catalyst exhibited good catalytic activity and gave higher % yield of the respective acetamides than S-MWCNT. This is attributed to higher surface acidity of S-MC, however the catalyst was found to be non-recyclable. S-MWCNT exhibited moderate % yield and 100% selectivity towards the formation of products. S-MWCNT catalyst was recycled up to 5 times with a consistent % yield of the respective acetamide derivatives. The synthesized acetamide derivatives were analyzed by M.P, ^{1}HNMR techniques.

Keywords: Multiwalled Carbon Nanotubes, Mesoporous Carbon, Acetamide Derivatives, Aromatic Amines, Aromatic Acids.

1. INTRODUCTION

Currently Nanotechnology is the most vital feature which involves integration of different branches of science and technology. In the present scenario of research and development synthesis, design and fabrication of nanostructured materials and tuning their materials properties known as nanoarchitectonics is employed in various fields.[1–5] Among different nanomaterials, nanocarbons such as graphene, carbon nanotubes and fullerenes are the most important representative allotropes which are employed for nanoarchitectronics in electronics, biomedical applications, drug delivery, bioimaging, sensors, batteries, energy storage systems, nanoelectrocatalysis and also in heterogeneous catalysis.[6–9]

In heterogeneous catalysis, carbon materials such as mesoporous carbon (MC), activated carbon (AC) as well as carbon nanotubes (CNTs) and their modified forms are commonly used as catalysts/supports in various organic transformations.[10] There are some unique properties of carbon materials which make them suitable for their application in numerous catalytic processes. These properties include (a) chemical stability or chemical inertness, (b) high specific area, (c) eco-friendly in nature, (d) their tunable porosity and unique surface chemistry. Since carbon materials are obtained in different forms such as tubes, fibers, granules, monoliths, fabrics and pellets, they can be conveniently used in various catalytic reactions.[11,12] Modification of carbon materials with anions, transition metals and transition metal oxides are widely studied and have exhibited good catalytic activity in many organic reactions such as alkylation,[13] condensation,[14] transesterification,[15] dimerization,[16] amidation,[17] benzylation[18] and esterification[19] etc.

In particular modified MC and CNTs are currently being used as catalysts supports in organic transformation reactions. Modified MC is known for its catalytic activity due

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to high surface area, large pore volume, optimal pore size and ordered pore structure. According to literature, Daiya Song et al.,[20] prepared aryl sulphonic acid functionalized MC and used in the synthesis of ethyl levulinate from levulinic acid and furfuryl alcohol. Lingtao[21] and his co-workers prepared phosphoric acid modified MC and used as novel solid acid catalysts in the synthesis of methyl oleate from oleic acid and methanol in esterification reaction. Another Interesting carbon material is CNTs which exhibits remarkable catalytic activity, when it is used as supports in organic reactions. This is attributed to its unique properties such as electrical and thermal conductivity; uniform pore size distribution, high length to diameter aspect ratio and high surface area.[22] Zhou et al.,[23] have prepared functionalized MWCNT supported TiO_2 and used it in the transesterification of dimethyl carbonate with phenol to synthesize methyl phenol carbonate. Xianbing et al.,[24] have modified MWCNT via carboxylic acid formation and studied esterification of glycerol with acetic acid. Further sulphuric acid modified MC and MWCNT are being developed as catalysts supports in the synthesis of organic fine chemicals due to easy separation and recovery from the reaction mixture as well as their convenient reusability was also reported.[25]

Amide formation is one of the most important reactions in pharmaceutical industry. The amide bond is a key functional group in organic chemistry. It plays an important role in the synthesis of wide range of chemicals including peptides, polymers, proteins and pharmaceutical agents. Keeping in view the importance of the above mentioned factors, we have modified MWCNT and MC with sulphuric acid by wet impregnation technique and used in the synthesis of various acetamide derivatives. Further catalytic activity studies and reusability of the catalysts were also investigated.

2. EXPERIMENTAL DETAILS

2.1. Materials

Multiwalled carbon nanotubes were procured from Nanocyl, Belgium, mesoporous carbon was obtained from Sigma Aldrich. Sulphuric acid, aniline, benzyl amine, para-chloro aniline, para-methoxy aniline, phenyl acetic acid, phenylthio acetic acid and Indole 3-acetic acid, ethyl acetate, sodium bicarbonate and petroleum ether were procured from Merck Pvt. India Ltd and used as received.

2.2. Preparation of Catalytic Materials

In a typical procedure of synthesis of sulphate modified carbon based catalysts supports, 3 g of commercially available multiwalled carbon nanotubes (MWCNT) and mesoporous carbon (MC) was weighed accurately and mixed well with 3 mL of 3 M H_2SO_4 in an agate mortar for 1 h. The obtained paste was dried in a hot air oven at 110 °C for 12 h. Further, catalytic materials were mixed well to get homogeneous powder. Sulphate modified MWCNT and MC are abbreviated as S-MWCNT and S-MC respectively.

2.3. Characterization of S-MWCNT and S-MC

The prepared catalytic materials were characterized by appropriate analytical techniques. Powder X-ray diffraction (Powder-XRD) patterns were recorded on a Panalytical Xpert pro X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm) in the 2θ range of 5° to 70° at 40 kV with a scanning rate of 2°/min. Brunauer, Emmett and Teller (BET) surface area was determined from Quantachrome Nova-1000 surface analyzer. Morphology and elemental composition of the materials were determined by Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM–EDS) techniques using Quanta 200 FEI instrument. Transmission Electron Microscopy (TEM) images were recorded on Tecnai instrument. Surface acidity of the materials was determined using Temperature-Programmed Desorption-Ammonia (TPD-NH_3) analyzer using Mayura analytical instrument as well as *n*-butyl amine back titration method.

2.4. Catalytic Activity Studies of S-MWCNT and S-MC

The catalytic activity of S-MWCNT and S-MC catalysts were investigated in the synthesis of acetamide derivatives using substituted aromatic amines (aniline, benzyl amine, para-chloro aniline and para-methoxy aniline) and aromatic acids (phenyl acetic acid, phenylthio acetic acid and Indole 3-acetic acid) in a liquid phase reaction. In a typical procedure of synthesis of acetamide derivatives, mixture of aromatic acid and substituted aromatic amine in 1:1 molar ratio was refluxed at 110 °C using 50 mg of catalyst with 10 mL of toluene as solvent in a 100 mL R B flask fitted with water cooled condenser. After a definite period of time, the reaction mixture was cooled to room temperature and filtered to separate the solid catalyst. The product was recovered from the filtrate using sodium bicarbonate and ethyl acetate. The separated acetamide derivative was confirmed from TLC, MP, ^{1}HNMR techniques. Further optimization of the reaction conditions was made by using different amounts of the catalysts, varying the temperature, duration of the reaction. The effect of different solvents in the synthesis of acetamide derivatives was also checked.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalysts

PXRD Analysis: Powder X-ray diffraction patterns of S-MWCNT and S-MC are given in Figure 1. MWCNT exhibited a strong symmetrical diffraction peak at $2\theta = 25°$. This 2θ value corresponds to diffraction from hexagonal (002) planes of graphitic structure of MWCNT (JCPDS car files, no 41-1487). The low intensity peak at 43.2° is

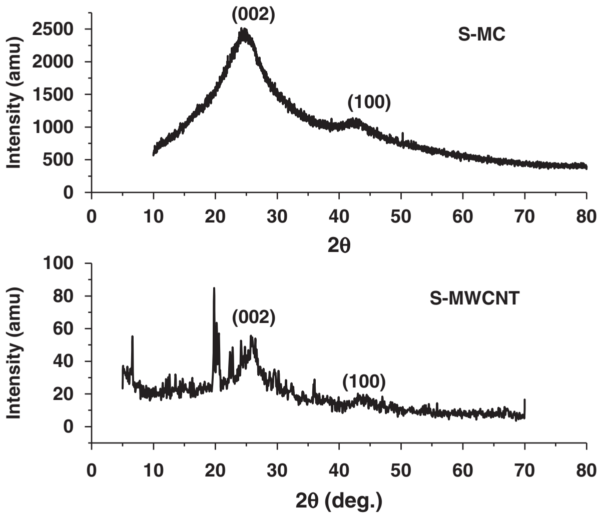


Figure 1. PXRD pattern of S-MWCNT and S-MC catalysts.

attributed to diffraction from (100) plane.[26] Similar observations were observed in case of MC catalysts. However after acid treatment, the diffraction pattern of S-MWCNT was considerably altered with respect to 2θ value and its intensity. After the acid treatment of S-MC, it was noticed that there was not much difference in the diffraction peaks observed for (002) and (100) planes. However the diffraction peaks at $2\theta = 25$ and 43.2° was slightly shifted.

BET surface area and surface acidity measurement: BET surface area, pore volume, pore diameter and surface acidity of S-MWCNT and S-MC are given in Table I. Surface area, pore volume of S-MWCNT values is higher than S-MC and pore diameter as well as surface acidity values are higher in S-MC. The higher surface acidity of S-MC may be due to interaction of sulphate groups with porous structure of MC.

TPD-NH_3 profile: Temperature programmed desorption of ammonia for S-MWCNT and S-MC are given in Figure 2, where these catalysts supports were subjected to heat treatment in the temperature range 50 °C to 600 °C. It has been reported that, NH_3 desorption peaks obtained for the catalysts in the range of 50 to 250 °C correspond to weakly acidic sites on their surface and moderate acetic sites within the range of 250 to 350 °C. Furthermore, NH_3 desorption peaks above 350 °C correspond to strongly acidic sites on the surface of the catalyst.[27] The ammonia desorption peak can therefore be used to represent the concentration of the acidic sites on the surface of a catalyst. The TPD-NH_3 profile of S-MC catalyst contained two desorption peaks in the ranges of 200–250 and 270–360 °C which indicated the presence of both weak and moderately strong acidic sites. In case of S-MWCNT catalyst, the TPD-NH_3 profile contained a desorption peak in the range of 300 to 400 °C which indicated the presence of strong acid sites.

Table I. BET surface area, pore volume, pore diameter and surface acidity of S-MWCNT and S-MC.

Catalyst name	Surface area m^2/g	Pore volume cc/g	Pore diameter Å	Surface acidity mmol/g (*)
S-MWCNT	53.64	0.18	13.91	0.82
S-MC	25.63	0.05	78.51	1.75

Note: *Total surface acidity of the catalysts were measured using *n*-butyl amine back titration method.

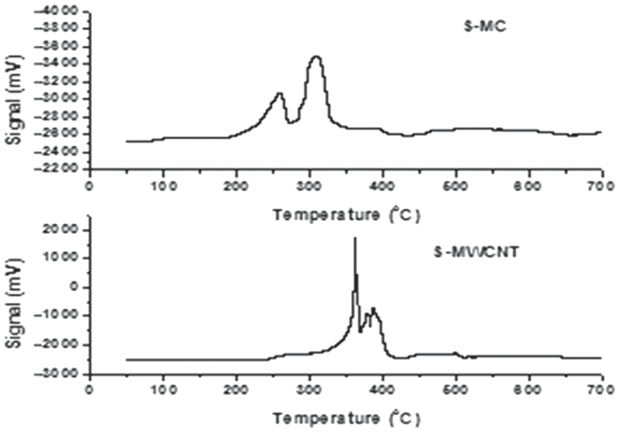


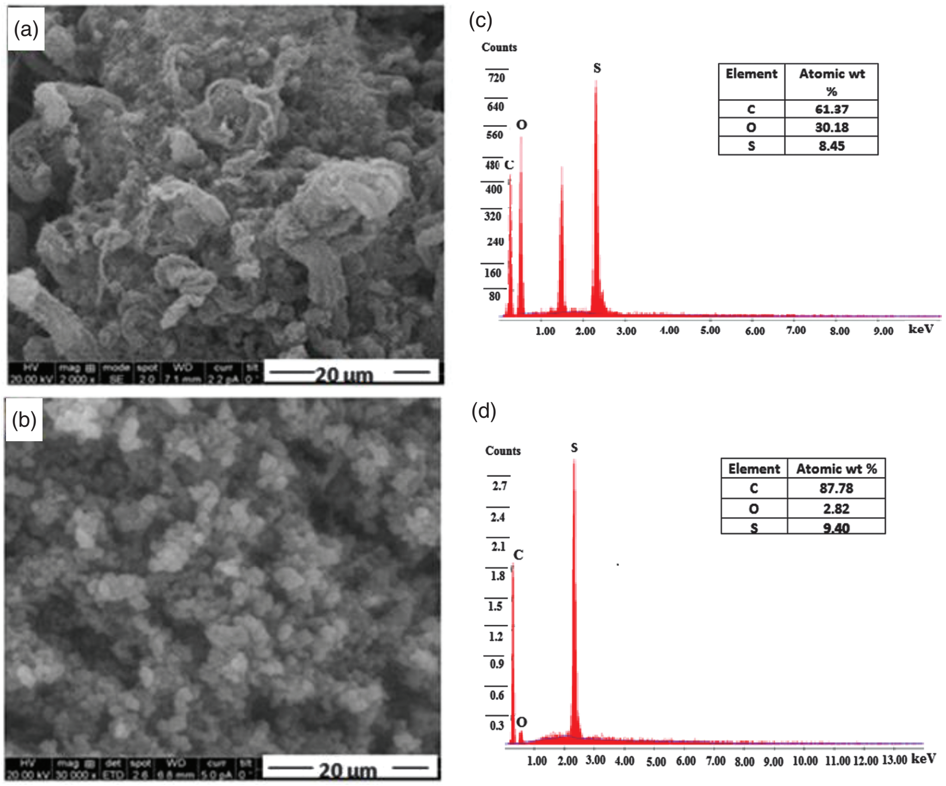
Figure 2. TPD-NH_3 profile of S-MWCNT and S-MC catalysts.

SEM images and EDS profiles: SEM images and the EDS profiles of S-MWCNT and S-MC are given in Figure 3. SEM images of S-MWCNT and S-MC revealed that, the catalytic materials retained their original structures as tubular (MWCNT) and spears (MC) with significant surface changes. The EDS profiles of S-MWCNT and S-MC show the presence of elemental sulphur as 8.45 and 9.40 atomic weight % respectively along with carbon and oxygen.

TEM images: The TEM images of S-MWCNT and S-MC catalysts are given in Figure 4. These images clearly indicate that the tubular structure of MWCNT is retained even upon sulphuric acid treatment. However the tubes in S-MWCNT are found to be thick due to acid treatment. In case of S-MC catalyst there is no significant difference in the structure but on the surface of mesoporous carbon black patches appeared due to acid treatment.

3.2. Catalytic Activity Studies

The catalytic activity of S-MWCNT and S-MC was investigated in the synthesis of acetamide derivatives using aromatic acids (phenyl acetic acid, phenylthio acetic acid and Indole 3-acetic acid) with substituted aromatic amines (aniline, benzyl amine, para-chloro aniline and para-methoxy aniline) in a liquid phase reaction (Table II). The obtained products were analyzed using NMR technique. The structural details of the obtained compounds are listed in Table II and it is matching with the reported literatures.[28–31]



Element	Atomic wt %
C	61.37
O	30.18
S	8.45

Element	Atomic wt %
C	87.78
O	2.82
S	9.40

Figure 3. SEM images of (a) S-MWCNT and (b) S-MC catalysts and EDS profiles of (c) S-MWCNT and (d) S-MC.

3.3. Spectral Data

1. *N-Diphenyl acetamide*: (Table II, entry 1): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 10.10 (s, 1H), 7.57 ($d, J = 8.0$ Hz, 2H), 7.31 − 7.19 (m, 7H), 7.09 ($t, J = 7.2$ Hz, 1H), 3.60 (s, 2H).

2. *N-benzyl-2-phenylacetamide*: (Table II, entry 2): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 8.50 (s, 1H), 7.30–7.14 (m, 10H), 4.24 (s, 2H), 3.29 (s, 2H).

3. *N-(4-chlorophenyl)-2-phenylacetamide*: (Table II, entry 3): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 8.53 (s, 1H), 7.39–7.19 (m, 9H), 4.22 (s, 2H).

4. *N-(4-methoxyphenyl)-2-phenylacetamide*: (Table II, entry 4): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 9.97 (s, 1H), 7.47 ($d, J = 9.2$ Hz, 2H), 7.29–7.20 (m, 5H), 6.84 ($d, J = 8.8$ Hz, 2H), 3.67 (s, 3H), 3.56 (s, 2H).

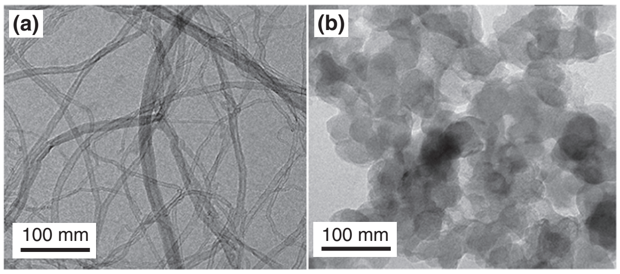


Figure 4. TEM images of (a) S-MWCNT and (b) S-MC catalysts.

5. *N-phenyl-2-(phenylthio)acetamide*: (Table II, entry 5): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 10.18 (s, 1H), 7.53 ($d, J = 7.2$ Hz, 2H), 7.38–7.25 (m, 6H), 7.19–7.15 (m, 1H), 7.03 ($t, J = 6.8$ Hz, 1H), 3.83 (s, 2H).

6. *N-benzyl-2-(phenylthio)acetamide*: (Table II, entry 6): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 8.59 (s, 1H), 7.34–7.23 (m, 6H), 7.21–7.12 (m, 4 Hz), 4.25 (s, 2H), 3.69 (s, 2H).

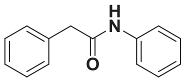
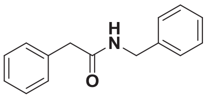
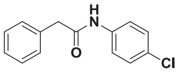
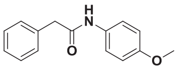
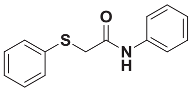
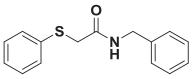
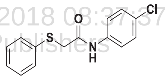
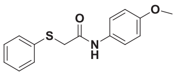
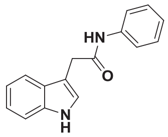
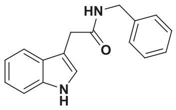
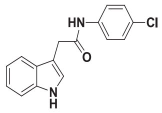
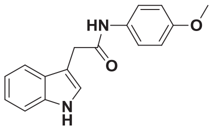
7. *N-(4-chlorophenyl)-2-(phenylthio) acetamide*: (Table II, entry 7): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 8.61 (s, 1H), 7.33–7.25 (m, 6 Hz), 7.19–7.12 (m, 3H) 4.23 (s, 2H), 3.68 (s, 2H).

8. *N-(4-methoxyphenyl)-2-(phenylthio) acetamide*: (Table II, entry 8): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 10.01 (s, 1H), 7.44 ($d, J = 6.8$ Hz, 2H), 7. 38 ($d, J = 1.6$ Hz, 2H), 7.30 ($t, J = 7.6$ Hz, 2H), 7.18 ($t, J = 7.6$ Hz, 1H), 6.88 ($d, J = 6.8$ Hz, 2H), 3.79 (s, 2H), 3.68 (s, 3H).

9. *2-(1H-indol-3-yl)- N-phenylacetamide*: (Table II, entry 9): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 10.88 (s, 1H), 10.06 (s, 1H), 7.59 ($d, J = 8.0$ Hz, 2H), 7.33 ($d, J = 8.0$ Hz, 1H), 7.27–7.20 (m, 3H), 7.06–6.93 (m, 3H), 3.70 (s, 2H).

10. *N-benzyl-2-(1H-indol-3-yl)acetamide*: (Table II, entry 10): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 10.84 (s, 1H), 8.37 (s. 1H), 7.53 ($d, J = 8.0$ Hz, 1H), 7.32 ($d, J = 8.0$ Hz, 1H), 7.27–7.17 (m, 6H), 7.06–7.02 (m, 1H), 6.96–6.92 (m, 1H), 4.25 (s, 2H), 3.55 (s, 2H).

Table II. Catalytic performance of S-MWCNT and S-MC in the amidation of acetamide derivatives from aromatic acids and substituted aromatic amines using 0.05 g of catalysts.

Entry	Aromatic acids	Aromatic amines	Acetamide derivatives	% yield S-MWCNT/MC
1	Phenyl acetic acid	Aniline	 *N*,2-diphenylacetamide	91/96
2		Benzyl amine	 *N*-benzyl-2-phenylacetamide	88/94
3		Para-chloro aniline	 *N*-(4-chlorophenyl)-2-phenylacetamide	68/73
4		Para-methoxy aniline	 *N*-(4-methoxyphenyl)-2-phenylacetamide	85/90
5	Phenylthio acetic acid	Aniline	 *N*-phenyl-2-(phenylthio)acetamide	89/93
6		Benzyl amine	 *N*-benzyl-2-(phenylthio)acetamide	82/88
7		Para-chloro aniline	 *N*-(4-chlorophenyl)-2-(phenylthio)acetamide	63/69
8		Para-methoxy aniline	 *N*-(4-methoxyphenyl)-2-(phenylthio)acetamide	80/86
9	Indole 3-acetic acid	Aniline	 2-(1*H*-indol-3-yl)-*N*-phenylacetamide	88/92
10		Benzyl amine	 *N*-benzyl-2-(1*H*-indol-3-yl)acetamide	87/91
11		Para-chloro aniline	 *N*-(4-chlorophenyl)-2-(1*H*-indol-3-yl)acetamide	65/70
12		Para-methoxy aniline	 2-(1*H*-indol-3-yl)-*N*-(4-methoxyphenyl)acetamide	83/91

11. *N-(4-chlorophenyl)-2-(1H-indol-3-yl)acetamide*: (Table II, entry 11): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 10.85 (s, 1H), 8.40 (s, 1H), 7.52 ($d, J = 8.0$ Hz, 1H), 7.33–7.29 (m, 3H), 7.23–7.16 (m, 3H), 7.06 ($t, J = 1.2$ Hz, 1H), 6.96 ($t, J = 1.2$ Hz, 1H), 3.55 (s, 2H).

12. *2-(1H-indol-3-yl)-N-(4-methoxyphenyl) acetamide*: (Table II, entry 1): ^{1}HNMR (400 MHz, DMSO-d$_6$): δ: 12.1 (s, 1H), 10.86 (s, 1H), 7.33 (2, $J = 8.4$ Hz, 2H), 7.21 ($d, J = 2.4$ Hz, 2H), 7.06–7.04 (m, 2H), 6.97–6.93 (m, 2H), 6. 83 ($d, J = 2.4$ Hz, 1H), 3.67 (s, 2H), 3.60 (s, 3H).

In general, the % yield of the acetamide derivatives obtained was very less when the reactions were carried out in the absence of the catalysts. Table II indicates amidation reactions carried out using different aromatic acids (phenyl acetic acid, phenylthio acetic acid and Indole 3-acetic acid) with substituted aromatic amines (1:1 molar ratio) and their % yield of the products using S-MWCNT and S-MC catalysts supports. It was noteworthy that S-MC gave higher % yield of acetamide derivatives irrespective of the different acids and amines used. Further aniline, benzyl amine and para methoxy aniline (electron donating group –OCH$_3$) with phenyl acetic acid gave highest % yield of respective products. On the other hand presence of electron-withdrawing substituent (i.e., Cl) on the aromatic ring of aniline gave low % yield of product (Table II, entry 3, 7 and 11).

Further experiments were carried out to evaluate the catalytic activity of the S-MWCNT and S-MC for the amidation of phenyl acetic acid and aniline in the synthesis of N,-diphenyl acetamide by changing the temperature, duration, amount of the catalysts and with different solvents. The effect of temperature and duration of the reaction with respect to % yield of N,-diphenyl acetamide was studied using S-MWCNT and S-MC catalysts (50 mg) and the results are given in Table III. The reaction did not proceed at room temperature. But it was observed that, the % yield of the product was increased with increase in the temperature from 70 to 110 °C and further remained same at 130 °C. The reactions were carried out using S-MWCNT and S-MC catalysts at different intervals of time such as 2, 4, 6, 8, 10 and 24 h and found highest % yield of product when the reaction was refluxed for 10 h. Further increase in the duration of the reaction from 10 to 24 h, there was no significant difference found in the % yield of the product.

Table III. Catalytic performance of S-MWCNT and S-MC catalysts at different temperature and duration of the reaction.

Catalysts	Reaction duration (h)	% Yield at 70 °C	% Yield at 90 °C	% Yield at 110 °C	% Yield at 130 °C
S-MC	2	0	0	0	0
	4	26	32	39	43
	6	44	47	59	62
	8	49	62	73	76
	10	**54**	**76**	**96**	**96**
	24	57	76	97	97.7
S-MWCNT	2	0	0	0	0
	4	22	28	36	38
	6	38	42	57	60
	8	44	56	69	71
	10	**50**	**70**	**91**	**91**
	24	53	74	91.8	92

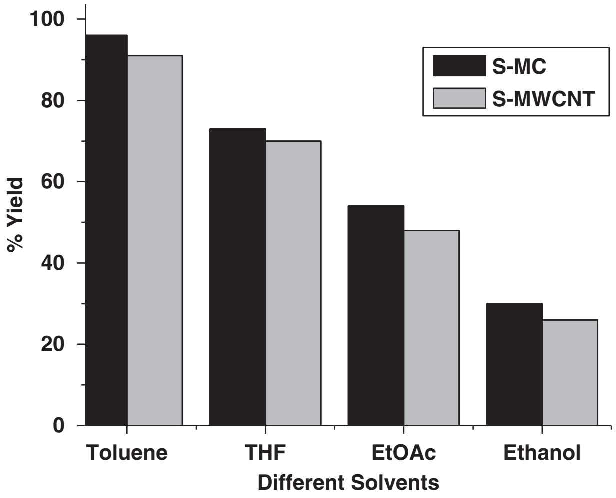


Figure 5. Catalytic performance of S-MWCNT and S-MC catalysts using 3(a) different solvents.

The study on the effect of solvents and amount of the catalysts in the synthesis of N,-diphenyl acetamide was performed using S-MWCNT and S-MC catalysts. The reaction was conducted in the presence of different solvents such as toluene, THF, ethyl acetate, and ethanol. Figure 5 indicates the % yield of N,-diphenyl acetamide using S-MWCNT and S-MC catalysts in the presence of different solvents. It is important to note that toluene gave highest % yield of N-diphenyl acetamide compare to other solvents using both the catalysts. This may be due to

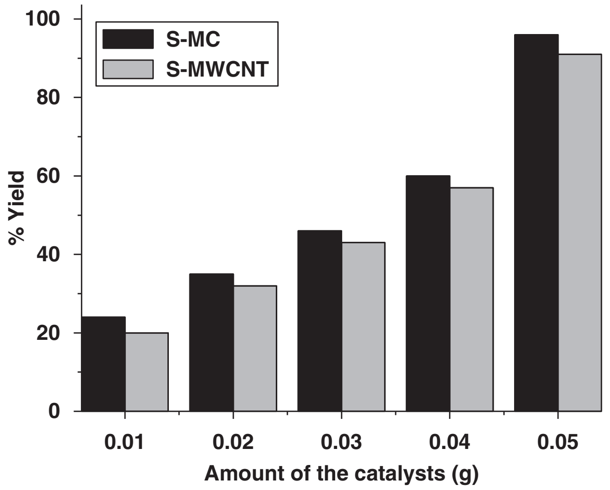


Figure 6. Catalytic performance of S-MWCNT and S-MC catalysts using different amount of catalysts.

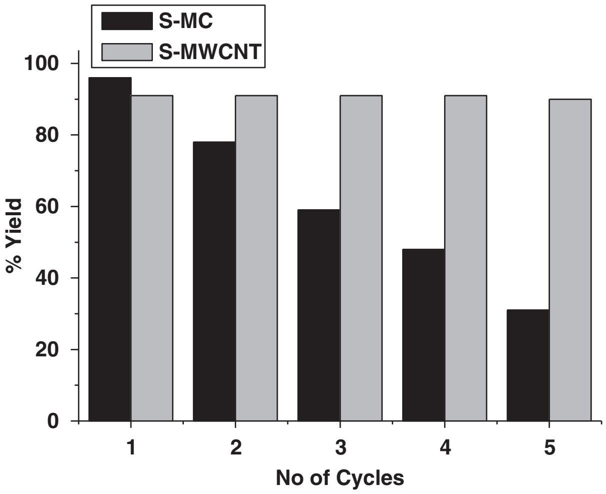


Figure 7. Reusability of S-MWCNT and S-MC catalysts in the amidation of *N*,-diphenyl acetamide from phenyl acetic acid and aniline.

the higher boiling point of toluene as compare to other solvents and also presence or absence of hydrogen bonding interactions between the amino groups and the solvents in the reaction mixture.[32]

The effect of amount of the catalyst was studied by varying the amount of the catalysts from 0.01 g to 0.05 g (Fig. 6). The results confirmed that the catalytic activity increases, when the amount of catalysts increases from 0.01 g to 0.05 g. Further increase in the amount of catalyst from 0.05 to 0.1 g, a less (~2%) increase in the % yield of the product was observed. Thus 0.05 g of catalyst was found to be optimum amount of catalyst for the reaction.

Reusability studies: Reusability of S-MWCNT and S-MC catalysts were investigated in the synthesis of *N*,-diphenyl acetamide at optimum reaction condition using 0.05 g catalysts at 110 °C for 10 (Fig. 7). Both S-MWCNT and S-MC were found to be reusable catalysts; however S-MWCNT was efficiently reused up to 5 times without losing its catalytic activity. During the catalysts reusability S-MWCNT was recovered easily and more efficiently than S-MC catalyst. Hence S-MWCNT catalyst was found to be a better reusable catalyst for the synthesis of *N*,-diphenyl acetamide via amidation reaction.

3.4. Mechanism of Amidation Reaction

A possible mechanism for the synthesis of *N*-diphenyl acetamide from phenyl acetic acid and aniline using S-MWCNT or S-MC are explained as follows (Fig. 8). Initially, acidic site of the catalyst reacts with oxygen of carbonyl group of phenyl acetic acids forming intermediate A. Protonation of the carbonyl oxygen by acidic catalyst makes the carbonyl carbon a much better electrophile, which reacts with aniline forming intermediate B. As the reaction precedes *N*-diphenyl acetamide (C) is obtained along with elimination of water molecule and the catalyst is regenerated.

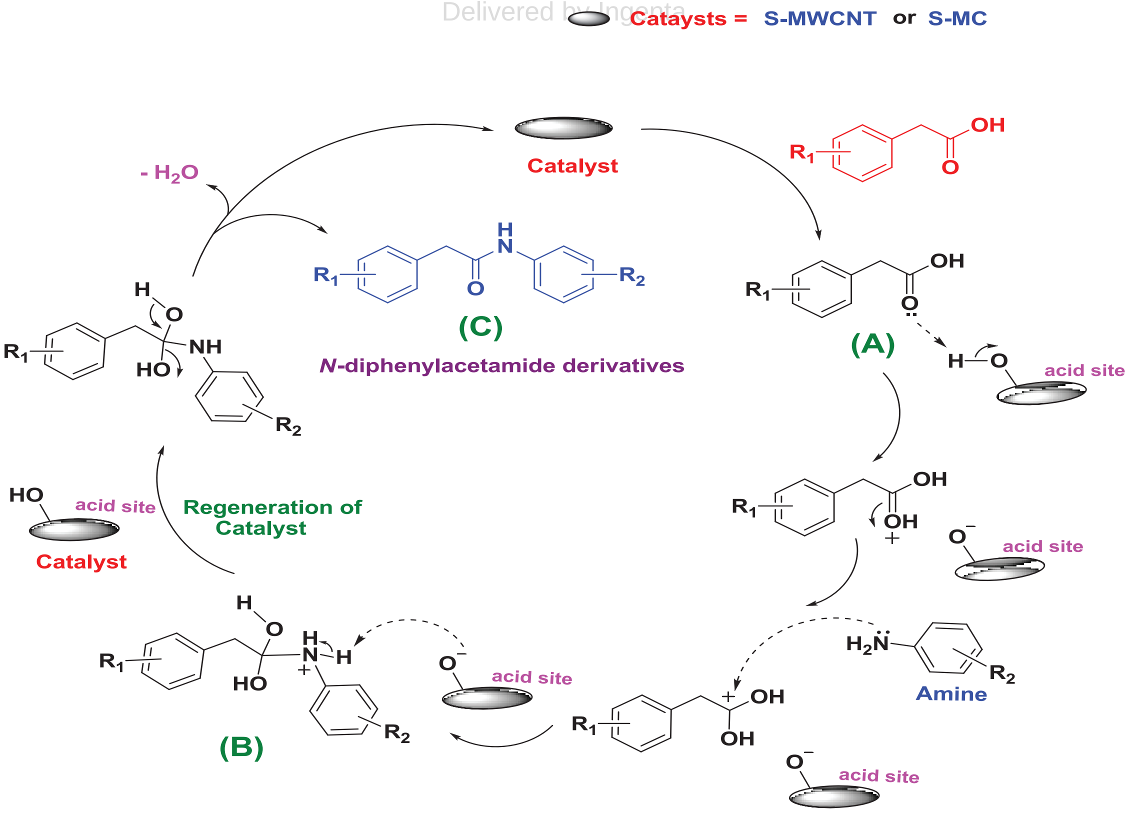


Figure 8. A plausible reaction mechanism for amidation of *N*-diphenyl acetamide from phenyl acetic acid and aniline.

4. CONCLUSION

Sulphuric acid modified MWCNT and MC have been investigated as solid acid heterogeneous catalysts for the synthesis of acetamide derivatives via amidation reaction. S-MWCNT and S-MC was found to be an efficient catalyst for the synthesis of acetamide derivatives with 100% selectivity and good yield. However, the catalytic activity of S-MC on the % yield of acetamide derivatives was found to be high as compare to S-MWCNT, this increase in activity due to surface acidity of S-MC (1.75 mmol/g) is more than the surface acidity of the S-MWCNT (0.82 mmol/g). Notably, the S-MWCNT catalyst was found to be recyclable up to five times without any loss in its catalytic activity, but in case of S-MC catalyst reusability was very poor. The results of amidation reaction from both the catalysts revealed that an electron donating group on the aromatic ring of aniline led to increase % yield of product, whereas yield decreases with electron withdrawing group (–Cl) on the aromatic ring of aniline.

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