Efficient and mild synthesis of pyrano-pyrimidines catalyzed by decorated multi-walled carbon nanotubes bearing cobalt, nickel and copper metals in water

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Abstract

Multicomponent reactions are reactions in which three or more are agreeable of raw interests, composed in a one-step chemical process and the product is formed they give. Since multivariate reactions are monovalent reactions and Single-step conversions to ideal synthesis are very close. In this research, one pot three components reaction was carried out between 1, 3-dimethylbarbituric acid, malononitrile and different aldehydes in the attendance of Cu/Co/Ni/MWCNTs as a recyclable catalyst. This catalyst indicated high catalytic actuality with good proficiency and reusable under mild reservation. This reaction is performed fine at ambient temperature. This method proposed numerous materials such as being environmentally amicable for short reaction times and creating high yield products. The catalysts were collected and specified with diversity spectroscopic, such as techniques, such as FT-IR, X-ray fracture, and scanning electron microscopy. After finalization of the reaction, the vintage was obsolete, purified and identified by the melting points, infrared spectroscopy (FT-IR) and the magnetic resonance of the hydrogen nucleus (^1H NMR) techniques.

1. Introduction

The progress of one-pot multicomponent reactions (MCRs) has possessed many notice from the superiority point of combinatory and medicinal chemistry [1, 2]. The finding of new synthetic methodologies to simplify the administration of involved organic combinations is an axial focal point of verification actuality in the field of novel organic chemistry[3, 4].Such a strategy proposition substantial advantages over contractual linear-type synthesis due to its flexible, convergent and atom impressive quiddity[2, 5].

Pyrano[2,3-d] pyrimidine can be prepared by the one-pot multicomponent synthesis of 1,3-dimethylbarbituric acid, various aldehydes and malononitrile[6–9].The different pyrano[2,3-d]pyrimidine derivatives that have been constitute so far indication interesting anti-tumor, cardiotonic, anti-bronchitis, and hepatoprotective. In Moreover, polyfunctionalized pyrano[2,3-d]pyrimidine formatives are joint constructive subunits in a nature of substantial intrinsic products[10–15].

Green chemistry has been a central topic in scientific and industrial research for centuries [16].The development of clean and environmentally friendly methods is the main objective of the synthesis of organic compounds. Organic solvents are often harmful because of this, as far as possible the use of them should be minimized. For example, the use of water as a reaction solvent is highly regarded because it is a highly polar green solvent and therefore immiscible with organic compounds. The reaction in the water media is generally a friendly environment and is devoid of any cancer effects that are very cheap and important in the industry [17–19].

CNTs are nanostructures with substantial electronic and mechanical properties. Since their detection in 1991[20, 21], they have possessed theoretical interest due to their unique structure and attributes. The panorama of uses has led to the prosperous functionalization of single-walled carbon nanotubes

(SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [22–27]. The MWCNTs are weighed as a nice support for heterogeneous catalysts by providing a great frame for the support and adherence for metal particles.

The oxidation process is one of the first reaction performed on carbon nanotubes, mainly for the purification and removal of catalysts [22, 28]. One of the methods to remove graphite plate and metal catalysts in carbon nanotubes is the use of acids [29–35].

2. Experimental Section

2.1. Materials and apparatus

All commercially available reagents were used, purchased from the Merck and Sigma-Aldrich Chemical Company in high purity. All of the reagents were used without any additional purification. If needed the products were purified via a thin-layer chromatography process to obtain the corresponding products in 69–98% yields. ^1H NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer with TMS as an internal reference. IR spectra were recorded as KBr pellets on a Nicolet FT-IR spectrophotometer. XRD patterns were reported by an X'Pert Pro (Philips) apparatus with 1.54 Å wavelengths of the X-ray beam and Cu anode material. The field emission scanning electron microscope (FE-SEM) of nanoparticles was performed on the Zeiss that operated at a 15 kV accelerating voltage. Thermogravimetric analysis (TGA) was performed on a mettler TA4000 system TG-50 at a heating rate of 10 K min⁻¹ under N₂ atmosphere. Melting points measured with Yanagimoto micro melting point equipment.

2.2. General procedure for preparation of Cu/Co/Ni/MWCNTs nanocatalyst

The MWCNTs (2.5 g) was added to the mixture of HNO₃ and H₂SO₄ (3:1) (40 ml). Then, 5 ml of ethanol was added drop by drop to the mixture on a stirrer. The mixture was then refluxed for 120 min. Afterwards the mixture was smoothed and dried for 2 h at 70°C. Then, 0.15 g of the activated MWCNTs were added to a blend of ethanol (10 mL), including 0.01 M CuCl₂ (30 mL) and buffer (pH 9.5; 30 mL). Slowly the formaldehyde (3 ml) added to the mixture on the ultrasonic bath for 2 h. After that it was smoothed and washed with water and acetone, and dried at 70°C for 3 h.

0.13 g of Cu/MWCNTs was added to the mixture of 0.01 M CoCl₂ (15 ml) and 0.01 M NiCl₂ (15 ml) and then ethanol (15 ml) and water (65 ml) were added. Slowly, 1M NaOH (15 ml) added to the mixture on the ultrasonic bath for 2 h and then was smoothed off, scoured with H₂O and acetone and dried at 80°C for 6 h.

2.3. General procedure for the synthesis of pyrano[2,3-d]pyrimidine

Aromatic aldehyde (1mmol), malononitrile (1.2 mmol), 1,3-dimethylbarbituric acid (1mmol), Cu/Co/Ni/MWCNTs catalyst (0.005g) in water (5ml) at room temperature. The improvement of the reaction was monitored by thin-layer chromatography (TLC). then conclusion of the reaction, ethyl acetate (10 ml) was added and the catalyst was detached by filtration. The organic layer was washed with ethanol (15 ml). The recovered catalyst was washed with ethanol and water and dried at 80 oC for major use.

2.4. Analytical data of selected compounds:

7-Amino-1,3-dimethyl-5-(4-nitrophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d] pyrimidine-6-carbonitrile (4a) ;White solid; m.p.: 227–228 °C (Lit. m.p 227–229 °C) [36]; IR (KBr) $\bar{\nu}$ = 3389, 3306, 3075, 2958, 2204, 1685, 1631, 1487, 1515,1382, 1230, 1186 ¹H NMR (400 MHz, DMSO) δ 3.10(3H, s, CH₃), 3.30(3H, s, CH₃), 4.50(1H, s, CH), 7.60(2H, d, *J* = 8 Hz, Ar-H), 8.15 (2H, d, *J* = 8 Hz Ar-H), 7.49(2H, s, NH₂)

7-Amino-5-(4-chlorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4b) ; White Crystal; m.p.: 234–235 °C (Lit. m.p 234–237 °C) [36]; IR (KBr) $\bar{\nu}$ = 3373, 3307, 3194, 2961, 2193, 1687, 1635, 1493, 1188, 1228, 835. ¹H NMR (400 MHz, DMSO) δ 3.07 (3H, s, CH₃), 3.34 (3H, s, CH₃), 4.34 (1H, s, CH), 7.25–7.28 (2H, d, *J* = 8 Hz, Ar-H), 7.31–7.36 (2H, d, *J* = 8 Hz, Ar-H), 7.36 (2H, s, NH₂).

7-Amino-5-(4-fluorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4c) ;White solid; m.p.: 225–226 °C (Lit. m.p 228–230 °C) [37]; IR (KBr) $\bar{\nu}$ = 3380,3307, 3185, 2958, 2196, 1686,1636 ,1526, 1233, 1193, 857. ¹H NMR (400 MHz, DMSO) δ 3.07 (3H, s, CH₃), 3.34 (3H, s, CH₃), 4.34 (1H, s, CH), 7.25 (2H, d, *J* = 8 Hz, Ar-H), 7.31 (2H, d, *J* = 8 Hz, Ar-H), 7.36 (2H, s, NH₂).

7-Amino-5-(4-methoxyphenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H- pyrano[2,3-d]-pyrimidine-6-carbonitrile (4d) ;White solid; m.p.: 280–284 °C (Lit. m.p 280 °C) [37]; IR (KBr) $\bar{\nu}$ = 3417,3302, 3189, 2946, 2192, 1700, 1638 ,1509, 1227, 1186, 847. ¹H NMR (400 MHz, DMSO) δ 3.01 (3H, s, CH₃), 3.03 (3H, s, CH₃), 3.54 (3H, s, CH₃), 4.30 (1H, s, CH), 6.56 (2H, d, *J* = 8 Hz, Ar-H), 7.15 (2H, d, *J* = 8 Hz, Ar-H), 7.30 (2H, s, NH₂).

7-Amino-5-(4-methylphenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4e) ; Yellow solid; m.p.: 226–227 °C (Lit. m.p 225 °C) [37]; IR (KBr) $\bar{\nu}$ = 3380,3310, 3200, 2923, 2199, 1687, 1640,1490, 1228, 1185, 832. ¹H NMR (400 MHz, DMSO) δ 2.25 (3H, s, CH₃), 3.10 (3H, s, CH₃), 3.35 (3H, s, CH₃), 4.25 (1H, s, CH), 7.10 (2H, d, *J* = 8 Hz, Ar-H), 7.10 (2H, d, *J* = 8 Hz, Ar-H), 7.30 (2H, s, NH₂).

7-Amino-5-(3-fluorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4f) ; White solid; m.p.: 227–229 °C (Lit. m.p 228–229 °C)[38]; IR (KBr) $\bar{\nu}$ = 3390,3314, 3197, 2965, 2201, 1688, 1642 ,1489, 1229, 1186. ¹H NMR (400 MHz, DMSO) δ 3.08 (3H, s, CH₃), 3.50 (3H, s, CH₃), 4.50 (1H, s, CH), 7.30 (1H,d, Ar-H), 7.00(2H, s, Ar-H), 7.00 (1H, t, *J* = 8 Hz, Ar-H), 7.00 (1H, d, *J* = 8 Hz, Ar-H), 7.40 (2H, s, NH₂).

7-Amino-5-(3-bromophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4g) ; White solid; m.p.: 216–218 °C (Lit. m.p: 218–219 °C) [39]; IR (KBr) $\tilde{\nu}$ = 3377, 3313, 3197, 2960, 2202, 1684, 1638, 1490, 1228, 1186, 1071. ¹H NMR (400 MHz, DMSO) δ 3.02 (3H, s, CH₃), 3.34 (3H, s, CH₃), 4.34 (1H, s, CH), 7.25 (2H, m, Ar-H), 7.40 (1H, m, Ar-H), 7.42 (2H, s, NH₂).

7-Amino-5-(3-methoxyphenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4h) ; White solid; m.p.: 200–206 °C (Lit. m.p: 200–206 °C) [7]; IR (KBr) $\tilde{\nu}$ = 3407, 3318, 3199, 2951, 2193, 1688, 1649, 1494, 1229, 1187, 746. ¹H NMR (400 MHz, DMSO) δ 3.08 (3H, s, CH₃), 3.34 (3H, s, CH₃), 3.72 (3H, s, CH₃), 4.30 (1H, s, CH), 6.72 (1H, s, Ar-H), 6.78 (2H, d, *J* = 8 Hz, Ar-H), 7.20 (1H, t, *J* = 8 Hz, Ar-H), 7.32 (2H, s, NH₂).

7-Amino-1,3-dimethyl-5-(3-nitrophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4i) ; White solid; m.p.: 255 – 226 °C (Lit. m.p 255 – 227 °C) [37]; IR (KBr) $\tilde{\nu}$ = 3430, 3333, 3185, 2952, 2195, 1695, 1650, 1492, 1520, 1389, 1231, 1188, 677, 776, 904. ¹H NMR (400 MHz, DMSO) δ 3.06 (3H, s, CH₃), 3.36 (3H, s, CH₃), 4.56 (1H, s, CH), 7.32 (2H, s, NH₂), 7.60 (1H, t, *J* = 8 Hz, Ar-H), 7.78 (1H, d, *J* = 8 Hz, Ar-H), 8.10 (1H, d, *J* = 8 Hz, Ar-H), 8.10 (1H, s, Ar-H).

7-Amino-5-(2-bromophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4j) ; white solid; m.p.: 237 °C (Lit. m.p: 237–238 °C) [38]; IR (KBr) $\tilde{\nu}$ = 3397, 3311, 3190, 2960, 2194, 1688, 1643, 1489, 1232, 1190, 1071. ¹H NMR (400 MHz, DMSO) δ 3.04 (3H, s, CH₃), 3.34 (3H, s, CH₃), 4.86 (1H, s, CH), 7.12 (1H, m, *J* = 8 Hz, Ar-H), 7.25 (1H, d, *J* = 8 Hz, Ar-H), 7.26 (1H, t, *J* = 8 Hz, Ar-H), 7.52 (1H, d, *J* = 8 Hz, Ar-H), 7.42 (2H, s, NH₂).

7-Amino-5-(2-fluorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4k) ; White solid; m.p.: 237–239 °C (Lit. m.p: 238–239 °C) [38]; IR (KBr) $\tilde{\nu}$ = 3380, 3308, 3185, 2959, 2197, 1689, 1639, 1497, 1233, 1193, 748. ¹H NMR (400 MHz, DMSO) δ 3.05 (3H, s, CH₃), 3.35 (3H, s, CH₃), 4.70 (1H, s, CH), 7.10 (1H, t, *J* = 8 Hz, Ar-H), 7.1 (1H, d, *J* = 8 Hz, Ar-H), 7.25 (1H, d, *J* = 8 Hz, Ar-H), 7.25 (1H, t, *J* = 8 Hz, Ar-H), 7.40 (2H, s, NH₂).

7-Amino-5-(2-methylphenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4l) ; White solid; m.p.: 247 °C (Lit. m.p: 247–248 °C) [40]; IR (KBr) $\tilde{\nu}$ = 3379, 3312, 3197, 2958, 2200, 1712, 1687, 1488, 1228, 1185, 751. ¹H NMR (400 MHz, DMSO) δ 2.26 (3H, s, CH₃), 3.06 (3H, s, CH₃), 3.34 (3H, s, CH₃), 4.26 (1H, s, CH), 7.00 (3H, m, Hz, Ar-H), 7.16 (1H, t, *J* = 8 Hz, Ar-H), 7.30 (2H, s, NH₂).

7-Amino-5-(2-chlorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4m) ; White solid; m.p.: 238–240 °C (Lit. m.p: 238–240 °C) [41]; IR (KBr) $\tilde{\nu}$ = 3395, 3312, 3192, 2957, 2194, 1689, 1642, 1487, 1232, 1190, 751. ¹H NMR (400 MHz, DMSO) δ 3.05 (3H, s, CH₃), 3.35 (3H, s, CH₃), 4.85 (1H, s, CH), 7.20 (4H, t, *J* = 8 Hz, Ar-H), 7.30 (2H, d, *J* = 8 Hz, Ar-H), 7.29–7.38 (2H, d, *J* = 8 Hz, Ar-H), 7.35 (2H, s, NH₂).

7-Amino-1,3-dimethyl-5-(2-nitrophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4n) ;White solid; m.p.: 213–215 °C (Lit. m.p 216 °C) [41]; IR (KBr) $\bar{\nu}$ = 3381, 3307, 3185, 2952, 2196, 1687, 1636, 1496, 1526, 1354, 1233, 1193, 747. ^1H NMR (400 MHz, DMSO) δ 3.00 (3H, s, CH₃), 3.31 (3H, s, CH₃), 5.15 (1H, s, CH), 7.42 (1H, t, J = 8 Hz, Ar-H), 7.51 (1H, d, J = 8 Hz Ar-H), 7.62 (1H, d, J = 8 Hz Ar-H), 7.82 (1H, d, J = 8 Hz Ar-H), 7.50 (2H, s, NH₂).

7-Amino-5-(2,6-dichlorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4o) ;White solid; m.p.: 243–244 °C (Lit. m.p 243–244 °C) [43]; IR (KBr) $\bar{\nu}$ = 3385, 3314, 3192, 3196, 2199, 1690, 1655, 1461, 1235, 1037, 755. ^1H NMR (400 MHz, DMSO) δ 3.04 (3H, s, CH₃), 3.34 (3H, s, CH₃), 5.38 (1H, s, CH), 7.26 (1H, t, J = 8 Hz, Ar-H), 7.34 (1H, d, J = 8 Hz, Ar-H), 7.46 (1H, d, J = 8 Hz, Ar-H) 7.46 (2H, s, NH₂).

7-Amino-5-(2,4-dichlorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4p) ;White solid; m.p.: 243–245 °C (Lit. m.p 243–246 °C) [43]; IR (KBr) $\bar{\nu}$ = 3391, 3310, 3192, 2960, 2195, 1690, 1640, 1461, 1228, 1186. ^1H NMR (400 MHz, DMSO) δ 3.02 (3H, s, CH₃), 3.34 (3H, s, CH₃), 4.84 (1H, s, CH), 7.32–7.38 (2H, m, Ar-H), 7.41 (1H, s, Ar-H), 7.41 (2H, s, NH₂).

7-Amino-5-(3,4,5-trimethoxyphenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4q) ; Yellow solid; m.p.: 177 °C ; IR (KBr) $\bar{\nu}$ = 3342, 3191, 2945, 2197, 1694, 1648, 1496, 1184, 1119. ^1H NMR (400 MHz, DMSO) δ 3.10 (3H, s, CH₃), 3.35 (3H, s, CH₃), 3.60 (3H, s, CH₃), 3.70 (6H, s, CH₃), 4.30 (1H, s, CH), 6.50 (2H, s, Ar-H), 7.30 (2H, s, NH₂).

7-Amino-1,3-dimethyl-2,4-dioxo-5-phenyl-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]-pyrimidine-6-carbonitrile (4r) ;White solid; m.p.: 259–260 °C (Lit. m.p 260–262 °C) [44]; IR (KBr) $\bar{\nu}$ = 3374, 3308, 3194, 2961, 2194, 1688, 1636, 1493, 1229, 1188. ^1H NMR (400 MHz, DMSO) δ 3.07 (3H, s, CH₃), 3.35 (3H, s, CH₃), 4.31 (1H, s, CH), 7.20 (5H, m, Hz Ar-H), 7.32 (2H, s, NH₂).

3. Results And Discussion

Preparation and characterization of catalyst

The functionalization of multi-walled carbon nanotubes was performed using two acids HNO₃ and H₂SO₄ under reflux conditions. In order to form the hydroxyl groups and carboxylic acid groups. The obtained structure was then activated by mixing of the Ni²⁺, Co²⁺ and Cu²⁺ metal ions (Fig.1).

The FT-IR spectra are related to the primary carbon nanotube (Fig.2a) and the oxidized carbon nanotube (Fig.2b). As shown in this Figure, due to the high symmetry of the initial nanotube, the weak absorption bands are seen in the spectrum. But in the oxidized, the absorption bands of 3600 cm⁻¹ related to the O-H band are shown. The absorption band appeared is about 1700 cm⁻¹ belonging to the C=O of carboxylic acid group. Another absorption band at 1200 cm⁻¹ can be corresponds to the C-O bond.

The activated crystalline structure of multi-walled carbon nanotubes, Cu/ MWCNTs and Cu/Co/Ni/MWCNTs was also studied by XRD characterization .The XRD pattern of MWCNTs, Cu/MWCNTs and Cu/Co/Ni/MWCNTs are shown in Fig. 3. The diffraction pattern of catalyst is in good agreement with the pattern of all reference compounds. Diagram A related to the functionalized carbon nanotube showing only the carbon-related peak of the multi-walled carbon nanotube. Diagram B is the step where only the Cu²⁺ metal is deposited on a multi-walled carbon nanotube and its peak is a peated in 36. The diagram C is about the final step of making a nanocatalyst, all three metals are well placed on a multi-walled carbon nanotube support.

The field emission scanning electron microscopy (FE-SEM) images of Cu/Co/Ni/MWCNTs nanocatalyst showed the level morphologies of the catalysts. Metal nanoparticles with particle sizes of 22 to 42 nm are well dispersed on the surface of multi-walled carbon nanotubes.

The EDX pattern of the Cu/Co/Ni/MWCNTs catalyst is shown in Fig.5. According to the analysis, the presence of nickel, copper, cobalt and oxygen atoms on the catalyst surface has been demonstrated. The presence of carbon as catalyst substrate has also been shown.

It can be seen from the TGA diagram that the first mass reduction at 200-300 °C is due to the removal of water and solvents from the pores of nanostructure. Decarboxylation of the carboxylic acid group also occurs in this fracture. At 750 °C, weight loss is also observed which is related to the destruction of carbon nanotubes and finally, 40% of the material still remains.

3.2. Investigation of catalytic activity

The catalytic performance of the synthesized Cu/Co/Ni/MWCNTs nanocatalysts was investigated in the organic reaction of pyrano[2,3-d]pyrimidine formation. The reaction between 1,3-dimethylbarbituric acid, malononitrile and aldehyde was selected as the model reaction. Finally, in order to optimize the factors conditions such as solvent, temperature and catalyst value were investigated. Low yields of the products were seen using toluene and DMF (Table 1, entries 5 and 4) and the H₂O was selected as the prime solvent for the model reaction at 25 °C (Table 1, entry 10) to produce pyrano[2,3-d] pyrimidine in excellent yield.

Table 1. Optimization of the reaction conditions ^a

Entry	Solvent	T(°C)	Catalyst(mg)	Time (min)	Yield (%)
1	EtOH	Reflux	0.05	120	88
2	CH ₃ CN	Reflux	0.05	240	70
3	DMSO	140	0.05	240	72
4	DMF	140	0.05	250	60
5	Toluene	110	0.005	200	68
6	H ₂ O	100	0.005	30	90
7	H ₂ O/EtOH	90	0.03	90	88
8	PEG	140	0.03	160	70
9	H ₂ O	80	0.03	40	88
10	H ₂ O	80	0.05	100	90
11	H ₂ O	25	0.005	8	98

^a Reaction conditions: aldehyde (1mmol), malononitril (1.2 mmol) and 1,3-dimethylbarbituric acid (1 mmol).

In order to investigate the further optimization of the catalyst synergy conditions, the reaction of pyrano[2,3-d] pyrimidines for several types of catalysts was investigated. For the reaction we used other catalysts such as Co/MWCNTs, Ni/MWCNTs, Co/Ni/MWCNTs, Ni/Cu/MWCNTs and Co/Cu/MWCNTs which resulted in lower yields. The resulting increase in the catalytic activity of Cu/Co/Ni/MWCNTs could be attributed to the synergistic catalytic effect between the metallic species.

The reaction of pyrano[2,3-d] pyrimidines was carried out after optimization of the conditions in the presence of Ni/Cu catalyst and achieved 90% yield after 10 minutes. In addition, the synthetic reaction of various pyrano[2,3-d] pyrimidines was carried out under optimum conditions. The products are obtained in excellent yield and short reaction times. Aromatic aldehydes that have an electron acceptor group have high efficiency. and the reaction complete in less time. On the one hand, the presence of electron-withdrawing substituents, such as nitro group, has a strong inactivation effect on the positive carbon of aldehydes.

The most basic properties of catalysts are their reusability which must be examined. The reusing of Cu/Co/Ni/MWCNTs catalysts in the reaction of pyrano[2, 3-d] pyrimidines was studied. The catalyst is easily separated by filtration by dissolving the reaction product in ethyl acetate. The recovered catalyst was washed 3 times with acetone and 3 times with water. The catalyst had not lost its function after six recovery stages and could be reused.

In conforming to the FE-SEM picture of the used catalyst after six recycles, no considerable mutation in morphology of the Cu/Co/Ni/MWCNTs catalyst from that of the new catalyst was identified (Fig.9).

According to the XRD image of the catalyst after six steps of recovery it can be seen that there is no jump to the primary catalyst (Fig.10).

Firstly, between the aromatic aldehyde (1a-1) and the malononitrile (b), the Knoevenagel condensation reaction occurs and gives an electrophilic olefin (c). In the next step 1, 3-dimethylbarbituric acid (i) attack on electrophilic olefin to give (d) which then tautomerize to give (e). The average (e) by intramolecular nucleophilic addition gives (f) which then converted to terminal production (4a-1) by intramolecular Thorpe-Ziegler reaction.

4. Conclusions

In summary, We prepared Cu/Co/Ni/MWCNTs from multi-walled carbon nanotubes and nickel, cobalt and copper as catalysts which was characterized using several techniques such as; IR spectroscopy, SEM, EDX analysis, and TGA analysis. We first performed the reaction of pyrano[2,3-d]pyrimidines with Cu/Co/Ni/MWCNTs catalyst. High efficiency, short reaction time, environmental solvent, ease of product separation, cost-effective catalyst, easy catalyst recovery are the advantages of this reaction. The synthesized compounds have high antimicrobial activity.

Declarations

Acknowledgments

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Tables

Due to technical limitations, Table 2 is only available as a download in the Supplemental Files section.

Figures

Figure 1

Preparation of the Cu/Co/Ni/MWCNTs catalyst

Figure 2

FT-IR spectra of)a) primary multi-walled carbon nanotube b) functionalized multi-walled carbon nanotube

Peak List	
00-008-0415; C	
01-080-1268; Cu O	
00-041-1390; Cu ₂ + 2 (C O ₃) (O H) ₂	
00-024-0523; Ni C O ₃ (H ₂ O) ₄ ! 1.5 H ₂ O	
00-027-0178; (Cu , Ni) ₂ C O ₃ (O H) ₂	
01-073-1704; Ni Co ₂ O ₄	

Figure 3

XRD pattern: (a) MWCNTs (b) Cu/MWCNTs (c) Cu/Co/Ni/ MWCNTs catalyst

Figure 4

FE-SEM images of Cu /Co/Ni/MWCNTs catalyst

Figure 5

EDS spectrum of the Cu/Co/Ni/MWCNTs catalyst

Figure 6

TGA analysis of Cu/Co/Ni/MWCNTs catalysts

Figure 7

Catalytic activity of disparate catalysts in the pyrano[2,3-d]pyrimidine formation reaction

Figure 8

The pyrano[2,3-d] pyrimidine formation of 1,3-dimethylbarbituric acid, aromatic aldehyde and malononitrile in the presence of reused Cu/Co/Ni/MWCNTs

Figure 9

The FE-SEM picture of the used catalyst after six recycles

Figure 10

The XRD image of the used catalyst after six recycles

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table2.docx](#)
- [Scheme1.png](#)
- [SaberiSI.pdf](#)