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WET ZINC OXIDE NANOPOWDER CATALYZED EFFICIENT CONVERSION OF ALDEHYDES INTO NITRILES UNDER SOLVENT-FREE CONDITIONS

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ABSTRACT

The solvent-free approach has been developed for the direct conversion of aldehydes into cyanides using wet zinc oxide nanopowder as a catalyst. The wetness of heterogeneous catalysts is established for the conversion. Compared with other catalytic methods, the current procedure has certain advantages such as short reaction time, high yield of products, solvent-free reaction conditions, non-toxic and commercially available catalyst. The catalyst was recovered by simple filtration and reused in three successive reactions.

Keywords: Solvent-free, Zinc Oxide, Nanopowder, Moisture, Aldehydes, Nitriles.

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INTRODUCTION

Nitriles are one of the important classes of organic compounds. They displayed a key role in the manufacture of dyes, pharmaceuticals, agrochemicals, bioactive natural products and functional materials.[1-2] In addition; these compounds are used for the preparation of amines, amides, carboxylic acids and nitrogen-containing heterocycles.[3] Besides, the cyano group itself is present in the biologically active compound, such as Citalopram (anti-depression drug), Letrazole (anti-estrogen drug), Periciazine (anti-psychotic drug) (Fig.-1), 5-lipoxygenase inhibitors and HIV protease inhibitors.[4-6]

Fig.-1: Some marketed Drugs containing Nitrile Functionality

A huge number of methods have been reported for the preparation of nitriles using a variety of reagents. The classical approaches involve Rosenmund-von Braun and Sandmeyer reactions, but these methods required functionalized starting material and stoichiometric quantity of copper (I) cyanide reagent.[7-11] These compounds are prepared on an industrial scale by ammoxidation of toluene derivatives.[12] However, this method is suitable only for a very short number of substituted toluenes, demands high reaction temperature and pressure, and the use of the large quantity of ammonia restricted its application. Recently, improved synthesis of nitriles starting from aldehydes has been reported using a variety of reagents and catalysts such as $PhI(OAc)_2$/SDS[13], KF/Al_2O_3/DMSO[14], KI/I_2–TBHP[15], NaN_3/TfOH[16], TEMPO/HNO_3/AcOH[17], HMD[18], CF_3-BHA/TFA[19], $NH_4OH.HCl$/DMSO[20], $EtOPOCl_2$/DBU[21], $TMSN_3/ZrCl_4$[22], CH_2Cl_2/TfOH,[23], visible light / Co @ g-C_3N_4[24] and Red mud/mw[25]. All these reported methods have one or other disadvantages, such as the use of expensive, toxic or corrosive reagents, use of volatile organic solvent, drastic reaction conditions, limited scope of the substrate, tedious workup procedure and unsatisfactory yields. Zinc oxide is an inexpensive, environmentally benign and abundantly available inorganic solid.[26] Commercially available zinc oxide nanopowder is non-toxic and found

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suitable for photocatalytic activity; it could be useful for the manufacture of future generation optoelectronic devices in the U.V region.[27-28] In the last decade, zinc oxide nano-particles have shown tremendous applications as a reusable heterogeneous catalyst for the various organic transformations.[29]

EXPERIMENTAL

The ZnO nanopowder (particle size <100 nm, surface area 10-25m^2/g) was purchased from Merck and used with no further purification. All reagents were purchased and used without refinement from Fluka. The physical constants (m.p/b.p) were taken in an open capillary tube and are not corrected. Thin-layer chromatography was performed on Merck silica gel plates and spot visualized by U.V. light or exposure to iodine vapors. NMR spectra were obtained using Varian Mercury YH-500 MHz spectrometer (^{1}H NMR at 500 MHz and ^{13}C NMR at 100 MHz) with TMS as an internal standard; coupling constants are measured in Hz. Infrared spectra were recorded on Shimadzu FT-IR Tracer-100 spectrometer scanning 32 times from 4000-400 cm $^{-1}$ at 2.5 cm^{-1} resolution.

General Procedure (2a – 2p)

Aldehyde (2 mmol), hydroxylamine hydrochloride (2.5 mmol), ZnO nanopowder 0.32g (20 mol %) and water (2 drops) was taken in a 50mL round bottom flask and stirred for 5 min. at room temperature. Then, the temperature was raised to 90^{0}C and maintained for the appropriate time (Table 2). The development of the reaction was monitored by TLC. After completion, the reaction mixture was extracted with dichloromethane (3×5mL), and the extract was washed with aq. $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 and removal of the solvent under reduced pressure furnished analytically pure product.

Spectroscopic Data of Synthesized Compounds

Benzonitirle (2a)

Colorless liquid; bp 190-192^{0}C(lit.[25] 187-190^{0}C); IR (Neat) 2229 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40-7.49m(2H, ArH), 7.55-7.71m(3H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134, 131, 127, 118, 112.

4-Chlorobenzonitrile(2b)

White solid; mp 90-91^{0}C(lit.[25] 91-193^{0}C); IR (Neat) 2230 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.66 d (J8.6 Hz, 2H, ArH),7.70-7.81d (J 8.9 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =139.1, 132.3, 128.7, 118.5, 111.3.

4-Nitrobenzonitrile(2c)

White solid; mp 149^{0}C (lit.[25]146-149^{0}C); IR (Neat) 2231 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.89-8.01 (d, J = 8.9 Hz, 2H, ArH),8.26-8.40 (d, J = 8.9 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =151.0, 132.9, 124.5, 118.3, 116.9

3-Nitrobenzonitrile(2d)

Yellow solid; mp114^{0}C(lit.[25] 115-117^{0}C); IR (Neat) 2234 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57-7.64m (3H,ArH),8.10s (1H, ArH);); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =150.0, 133.0, 125.1, 118.2, 117.1.

3-Chlorobenzonitrile(2e)

Pale yellow solid; mp 44-46 ^{0}C(lit.[25] 43-46^{0}C); IR (Neat) 2225 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.48-7.53m (2H, ArH),7.73-7.78m (2H, ArH)); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =139.4, 133.3, 129.5, 118.1, 110.3.

4-Brobenzonitrile(2f)

White solid; mp 114-115^{0}C (lit.[13]115-117^{0}C); IR (Neat) 2227 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.79-7.91d (J 8.8 Hz, 2H, ArH),8.01-8.25d (J 8.8 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =134.2, 132.7, 128.1, 118.2, 112.

2-Hhydroxybenzonitrile(2g)

Colorless solid; mp 90-92 ^{0}C (lit.[31] 96 ^{0}C); IR (Neat) 2234 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.95-7.03m (2H, ArH),7.63-7.79m (2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =160.1, 134.2, 119.1, 116.3, 103.1.

2-Hhydroxy-3-methoxy-benzonitrile (2h)

Solid; mp57-58 ^{0}C (lit.^{16}55-57^{0}C); IR (Neat) 2234 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.02s(3H, Ar-OCH_3),7.30-7.36m (2H, ArH), 8.79s (1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =153.3, 146.7, 145.0, 125.1, 123.5, 117.3, 112.1, 57.3.

4-Methylbenzotitile(2i)

White solid; mp34-35^{0}C (lit.^{16}27-29^{0}C); IR (Neat) 2226 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ =2.79s (3H, Ar- CH_3), 7.7.30-7.34d (J 8.4 Hz, 2H, ArH),7.54-7.58 d (J 8.4 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =144, 132, 119.2, 109.2, 21.9.

4-Methoxybenzotitile(2j)

Colorless solid; mp 56-57^{0}C (lit.^{25} 57-59^{0}C); IR (Neat) 2225 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.94 s (3H, Ar- OCH_3), 7.01 d (J 8.2 Hz, 2H, ArH),7.67 d (J 8.2 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =162.7, 132, 119.1, 115, 133.7, 54.9.

Cinnamonitrile(2k)

Colorless oil; bp254-257^{0}C (lit.^{13}251-252^{0}C); IR (Neat) 2204 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ =6.98d(J 9Hz,2H, ArH), 7.28-7.36 m(3H, ArH), 7.49 d(J 15.9 Hz,1H, =CH), 7.78 d(J 15.9 Hz,1H,=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =150.7, 133.2, 131.5, 129.2, 127.3, 118.5, 96.2.

Thiophene-2-carbonitrile(2l)

Colorless liquid; bp 188-190^{0}C (lit.^{25} 134^{0}C); IR (Neat) 2206 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.20-7.25m (1H,ArH), 7.67-7.75m (2H,ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.2, 133.1, 127.5, 117.0, 114.5, 109.1.

3-Pyridinecarbonitrile(2m)

Faint yellow solid; mp 50^{0}C(lit.^{25} 50^{0}C); IR (Neat) 2230 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.82m (3H,ArH), 8.96 m(1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =152.9, 152.7, 138.9, 124.0, 117.1, 110.2.

1-Naphthonitrile(2n)

Faint yellow solid; mp 33-35^{0}C (lit.^{25} 115-117^{0}C); IR (Neat) 2224 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ =7.73-7.81m(4H, ArH), 7.94-8.02 m(3H,ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =133.5, 132.7,132.2, 132.0, 128.4, 127.7, 125.0, 124.7, 117.9, 110.4.

Butanenitrile(2o)

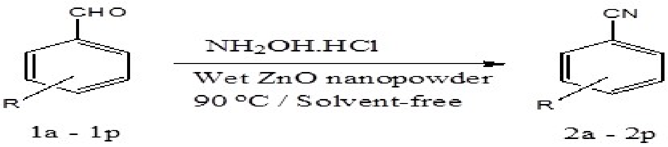
Colorless liquid; bp 118-119^{0}C (lit.^{31}118^{0}C); IR (Neat) 2246 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.96 t (J 2.8Hz,3H, CH_3), 1.75 m (2H, CH_2), 2.35 t(J2.8 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 118.9, 26.0, 25.1, 21.3.

2-Methylpropanenitrile(2p)

Colorless liquid; bp 106-108^{0}C (lit.^{13}108-109^{0}C); IR (Neat) 2248 cm^{-1}; ^{1}H NMR ($CDCl_3$,500 MHz): δ = 1.08 d (J2.9 Hz, 6H, $2CH_3$), 2.43m (1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ =119.0, 26.3, 25.0, 21.9.

RESULTS AND DISCUSSION

In this protocol, we report the one-pot conversion of aldehydes into nitriles in the presence of catalyst wet zinc oxide nanopowder (ZnO-Np) under solvent-free conditions (Scheme-1). In the initial experiments, we optimized the reaction conditions using ZnO-Np as a catalyst. The reaction between 4-methoxy benzaldehyde (2 mmol) and hydroxylamine hydrochloride (2.5 mmol) was chosen as a model reaction. The results obtained were recorded in Table-1. When the reaction mixture was stirred at 70^{0}C for 5 hours in an organic reaction medium such as acetonitrile, toluene and dichloromethane furnished a very low yield of the desired product (Table-1 entries 1, 2 and 3). The use of water as solvent at 90^{0}C improved the yield but a large amount of aldehyde was recovered unreacted (Table-1 entries 4 and 5). We previously reported that ZnO was effective for the synthesis of chalcones and thiol esters under solvent-free conditions.[30-31] Therefore; we aimed at ZnO-Np as a catalyst for this experiment. Then, we attempted to carry out the reaction under solvent-free conditions at 90^0C.The result showed that 20 mol% of ZnO-Np, in presence of two drops of water provides a 94% yield of desired product within a short reaction time (Table-1 entry 8). The additional increase in the amount of catalyst ZnO-Np up to 40mol % did not have any significant effect on the product yield or reaction time (Table 1 entry 9 and 10). The incipient moisture could easily release HCl free from hydroxylamine hydrochloride to dehydrate aldoxime on the surface of a heterogeneous catalyst.



Scheme-1

Table-1: Optimization of Reaction Conditions

Entry	Catalyst (mol %)	Solvent	Temperature (^{O}C)	Time (min.)	Yield^{a}(%)
1	20	CH_3CN	70	300	20
2	20	$PhCH_3$	70	300	10
3	20	CH_2Cl_2	70	300	15
4	20	H_2O	90	300	48
5	40	H_2O	90	300	47
6	20	---	90	45	68
7	30	---	90	45	70
8	20	---	90	45	94^{b}
9	30	---	90	45	94^{b}
10	40	---	90	45	93^{b}

[a]Isolated yield. [b]Reactions were carried out using 4-methoxy benzaldehyde (2 mmol), hydroxylamine hydrochloride (2.5 mmol), catalyst (ZnO-Np) and two drops of water.

After determining the best possible reaction conditions, we then examined the scope of reaction for the synthesis of nitriles using various aldehydes. The results are summarized in Table-2. Both aromatic and heteroaromatic aldehydes underwent smooth conversion to give a high yield of products in a short reaction time. However, aliphatic aldehydes provided a lower yield as compared with aromatic aldehydes. All activated (Table-2 entries g, h, i and j) and deactivated (Table-2 entries b, c, d, e and f) aromatic aldehydes reacted rapidly to furnish corresponding nitriles with excellent yield. The reaction products are clean required no chromatographic separation except in few cases (Table 2 entries o and p). It is noteworthy to mention that our one-pot procedure does not require corrosive CH_3COCl as observed in dehydration of aldoximes[32] or reflux in an organic solvent like DMF for 2.30 to 6 hours.

Moreover, the reusability of the catalysis was examined using model reaction for the synthesis of 4-methoxy benzonitirle. The catalyst was separated by simple filtration after each reaction, washed with CH_2Cl_2, dried in an oven at 100^{o}C and tested for activity in the subsequent reaction. It was found that the catalyst could be recycled and reusable three times without loss of activity.

Comparison of the effectiveness of wet ZnO-Np catalysts with reported catalysts is shown in Table-3. As compared to reported methods involving the use of hazardous catalyst under volatile reaction medium[13-15, 19] the present methodology is superior as excellent yield of products are obtained in short reaction time under solvent-free conditions. Some methods have reported a good yield of products at room temperature.[21-24] However, the requirement of toxic volatile organic solvent and high reaction time are the weaknesses of these methods.

Table-2: Synthesis of Nitriles 2a – 2p under aqueous under Solvent-free Conditions[a]

Entry	Aldehyde (1)	Product (2)	Time (min.)	Yield (%)^{b}
a	C_6H_5-CHO	2a	48	92
b	4-(Cl)-C_6H_4-CHO	2b	40	93
c	4-(NO_2)- C_6H_4-CHO	2c	35	95
d	3-(NO_2)- C_6H_4-CHO	2d	50	92
e	3-(Cl)- C_6H_4-CHO	2e	45	90

f	4-(Br)- C_6H_4-CHO	2f	35	94
g	2-(OH)- C_6H_4-CHO	2g	45	90
h	2-(OH),3-(OCH_3)- C_6H_3-CHO	2h	48	90
i	4-(CH_3)- C_6H_4-CHO	2i	40	95
j	4-(OCH_3)- C_6H_4-CHO	2j	45	94
k	C_6H_4-CH=CH-CHO	2k	50	91
l	Thiophene-2-carboxaldehyde	2l	50	88
m	3-Pyridinecarboxaldehyde	2m	52	91
n	1-Naphthaldehyde	2n	50	90
o	Butyraldehyde	2o	80	75
p	Isobutyraldehyde	2p	90	70

[a]Reactions were carried out using aldehyde (2 mmol), hydroxylamine hydrochloride (2.5 mmol), ZnO-Np (20 mol%)and two drops of water. [b]Yield of isolated products.

Table-3: Comparison of wet ZnONanopowder as a Catalyst with reported Catalytic Methods

Entry	Catalyst/Solvent	Temp. (^{0}C)	Time (h)	Yield (%)
1	$PhI(OAc)_2$/SDS	70	1-8	95[13]
2	KF/Al_2O_3/DMSO	100	4.5-10.5	91[14]
3	KI/I_2–TBHP	60	15	87[15]
4	TEMPO/HNO_3/AcOH	50	12	91[17]
5	CF_3-BHA/TFA/DME	80	-	92[19]
6	CH_2Cl_2/TfOH	r.t.	24	93[23]
7	$TMSN_3/ZrCl_4/CH_3CN$	r.t.	24	95[22]
8	$EtOPOCl_2$/ CH_2Cl_2,DBU/M.S.	r.t.	15	96[21]
9	Co @ g-C_3N_4/MeOH-H_2O	r.t.	14-20	92[24]
10	Wet ZnO-Np/solvent-free	90	0.35-1.30	95[This method]

All synthesized nitrile products **2a-p** were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopic methods. The spectral data of almost all synthesized compounds has supported the conversion of aldehydes to nitriles. For instance, compound **2p** was characterized by its ^{13}C NMR spectrum which showed characteristics –CN carbon at δ119.0 ppm which was further confirmed by the IR absorption band at 2248 cm^{-1}. Moreover, the absence of a peak at δ 9-10ppm due to –CHO proton in the ^{1}H NMR spectra of target compounds **2a-p** indicated the completion of the conversion.

CONCLUSION

In conclusion, we have developed a simple and competent protocol for the synthesis of nitriles using commercially available, low-cost and environmentally friendly zinc oxide nanopowder as a catalyst under thermal and solvent-free conditions. The advantages of this one-step environmentally benign procedure are recovery and reuse of catalyst, solvent-free reaction conditions and excellent yield of products in a short reaction time.

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