

Research Article

Synthesis of 9, 9, 10, 10 tetracyanonaphthaquinodimethane using Heterogeneous Catalyst

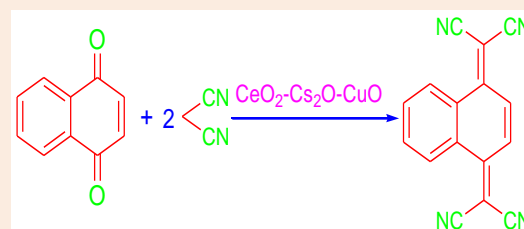
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Abstract

We report here synthetic strategy of 9, 9, 10, 10 tetracyanonaphthaquinodimethane by using SnO_2 and CeO_2 - Cs_2O - CuO mixed metal oxide as catalyst. This material was characterized by XRD, SEM, EDS and BET surface area. Oxidation and condensation two step reactions was constructed to prepared material. The SnO_2 was used for the oxidation of 1-naphthol (HCl , H_2O_2) in an acetonitrile as a solvent system for the reaction and CeO_2 - Cs_2O - CuO used for selective condensation. Moreover, this protocol has several advantages such as non-toxic, clean, easy separation of catalyst, recycle from the reaction medium.

Keywords: SnO_2 , Oxidation, CeO_2 - Cs_2O - CuO , Condensation



Graphic for Abstract

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Introduction

Generally cation, neutral radical and anion are thermodynamically stable redox species, these are observed in TCNQ [1]. There interesting phenomenon urges researchers to do investigation of organic products such as not only organic magnets but also organic conductors. For this purpose, it necessary to provide an organic compound which has electronic conductivity substantially equal to metals, and the molecules of this can be arranged in regular fashion. The synthesis of 9, 9, 10, 10 tetracyanonaphthaquinodimethane as a π acceptor has been investigated intensively because of their promising applications. Such as synthesis of charge transfer complexes [2]. The complexes of TCNQ containing as ligand with various metals show different properties having applications in optical recording disks [3], corrosion inhibition [4], solar energy collector [5], antibacterial agent [6], photoactive materials [7] and molecular active devices [8]. To synthesis of microelectronics material these type of material is utilized.

A few reports have appeared focusing on synthesis strategy like Acker *et al* [9], is a pioneer for the investigation of 7,7,8,8 TCNQ in 1962 this procedure relatively scarce when applied to large scale. Torres *et al* [10], reported synthesis of 6-hydroxymethyl 9, 9, 10, 10 tetracyanonaphthaquinodimethane (HMTCNAQ) number of steps with the addition of different type of reagents show complicated route. Baghdachi *et al* [11], synthesized 7,7,8,8 tetracyano-p-quinodimethaneacetic and propionic acids had not explicitly say about the high yields. Robert *et al* [12], discussed that the synthesis of monosubstitued TCNQ by using metal ammonia reduction/hydrolysis, the process was very tedious and large number of steps. Crawford *et al* [13], do elegant work for the increases the yield in molar quantities but its time consuming due to large steps.

In the recent years uses of heterogeneous catalyst in organic synthesis increases. Generally mixed metal oxides i.e. solid heterogeneous catalyst used for synthesis because of its advantageous properties like eco-friendliness, high stability and reusable than homogeneous catalyst. The oxide CuO , Cs_2O and CeO_2 were commonly used in the various reactions like oxidation [14], reduction [15], cyclization [16], condensation [17], photo catalytic reactions

[18], and dehydrogenation [19]. In present study, we have used SnO_2 for the synthesis of naphthalene-1, 4- dione by oxidation process. The synthesized mixed metal oxides $\text{CeO}_2\text{-Cs}_2\text{O-CuO}$ is prepared by co-precipitation method and to check its catalytic activity for the synthesis of 9, 9, 10, 10 tetracyanonaphthoquinodimethane. Moreover, our synthesized catalyst was noncorrosive, economical, nontoxic and easily collectable from the reaction medium.

Experimental

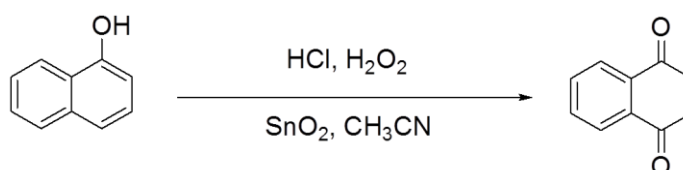
The starting materials were purchase from Aldrich and Fluka and used without purification. The melting points of products were taken in paraffin bath open capillary. The reaction progresses were check by TLC. The range of Fourier transform infrared spectra is 400 to 4000 cm^{-1} was recorded on JASCO FTIR/4100, Japan. ^1H NMR spectra on 300 MHz FT-NMR spectrometer in solvent CDCl_3 recorded.

Synthesis of catalyst

A simple and less expensive co-precipitation method were used for the synthesis of series $\text{CeO}_2\text{-Cs}_2\text{O-CuO}$ of mixed metal oxide. The required quantity of ammonium ceric nitrate, cesium nitrate, and copper nitrate were dissolved in deionised water separately and prepared clear solutions. These solutions are mixed together, with vigorous and constant stirring at 1h after the addition of 20 mL of 5% cetyl-trimethyl ammonium bromide (CTAB) as a structure directing agent. Add the 1:1 aqueous ammonia solution up to the pH 9 with stirring to obtain precipitate. Digest this precipitate in an electric oven at 60°C for 24h. The resulting precipitate not only filtered but also washed with deionized water, dried at 120°C for 12 h. Finally, calcined these powders at 500°C for 1h in an atmosphere. Repeat this procedure for all pure single and mixed metal oxide.

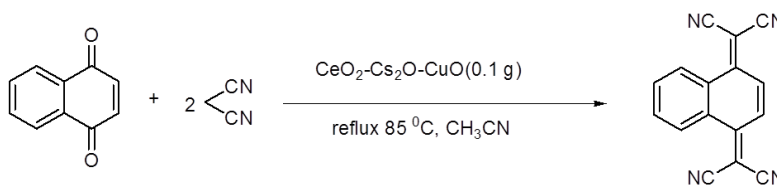
General method for the synthesis of 9, 9, 10, 10 tetracyanonaphthoquinodimethane.

In first step to take a mixture of α -Naphthol (7 mmol) in iodine flask. Then HCl 12 mL and H_2O_2 25 mL was added in 30 mL of acetonitrile. The reaction carried out under the sonication for 5 min. After addition of SnO_2 (0.1g), yellow colored product was obtained within 30 minutes at temperature 5 to 10°C . The product was poured on ice cold water and separates elusive intermediate using vacuum pump, wash with distilled water. To obtained naphthalene-1, 4- dione (Scheme 1).



Scheme 1

After that a mixture of naphthalene-1, 4- dione (1 mmol) and malononitrile (2 mmol) and $\text{CeO}_2\text{-Cs}_2\text{O-CuO}$ catalyst (0.1g) refluxed for 3 h at the temperature 85°C by using the solvent acetonitrile monitored by TLC. The reaction mixture filter though a filter paper, catalyst was separate out by evaporate acetonitrile naturally the blackish 9, 9, 10, 10 tetracyanonaphthoquinodimethane product was obtained (Scheme 2).



Scheme 2

Results and Discussion

For the synthesis of naphthalene 1, 4-dione. We proceeded to this reaction without catalyst but product is not obtained in acetonitrile, as reported 2-chloro naphthalene-1, 4-dione [20] as well as in ethanol. Then SnO₂ used as catalyst for the oxidation of α -Naphthol in ethanol unfortunately ungratified results were obtained means α -Naphthol is not oxidized at all. But in acetonitrile the product was obtained (**Table 1**). Used SnO₂ oxide, synthesized by Co-precipitation method. The selective only one (55%) product was obtained without applying any type of pressure and 45% unreacted α -Naphthol is remaining in the reaction. The role of SnO₂, to enhance the rate of this reaction and the product obtained in 30 mins selectively (**scheme 1**).

Table 1 Effect of various solvents and SnO₂ on the synthesis of naphthalene-1, 4-Dione^a

Entry	Time(min.)	Solvent	Catalyst	^b Product
1	60	CH ₃ CN	-----	^c NP
2	60	EtOH	-----	NP
3	60	EtOH	SnO ₂	NP
4	30	CH ₃ CN	SnO ₂	55%

^aReaction condition: α -Naphthol (7 mmol), HCl 12 mL, H₂O₂ 25 mL, SnO₂ (0.1g) carried out in sonicator in 30 mL CH₃CN. ^bIsolated yield. ^c no product.

To study the role of catalyst in scheme 2, Setup the reaction without catalyst and with using single metal oxides no result obtained (**Table 2**). But after the mixing of the metal oxides to formed CeO₂-Cs₂O-CuO by co-precipitation method, utilized in the same reaction to obtained 85% yield and 15% unreacted malononitrile is remaining. Literature survey reveals that the malononitrile would possibility to react at third position of naphthalene-1, 4- dione [21]. Because of catalyst selectivity, it react with the carbonyl group of the naphthalene 1, 4-dione to investigate 9, 9, 10, 10 tetracyanonaphthoquinodimethane (**Scheme 2**).

Table 2 Role of various metal oxides for the synthesis of 9, 9, 10, 10 tetracyano naphthoquinodimethane^a

Entry	Catalyst	Time(hr)	^b Yield%
1	--	3	^c NP
2	CeO ₂	3	NP
3	Cs ₂ O	3	NP
4	CuO	3	NP
5	CeO ₂ -Cs ₂ O-CuO	3	85%

^aReaction conditions: 2-methyl naphthalene-1, 4- dione (1 mmol),malononitrile(2 mmol),catalyst was refluxed in 15 mL CH₃CN. ^b Isolated yields ^c no product=NP.

Spectral data of representative compound

Naphthalene-1, 4- dione.

Yellow color; Yield 55%, M.P.105-108°C; IR (KBr) cm⁻¹: 1591, 1668, 1786; ¹H-NMR (CDCl₃): δ = 7.27 (s, 1H,CH), 7.81(d,1H,CH) and 8.20 (d, 1H, CH).

9, 9, 10, 10 tetracyanonaphthoquinodimethane

Blackish color; M.P.178-180°C ;). IR (KBr): 2216, 1556, 3072; ¹H NMR (CDCl₃): δ = 7.23 (d, 2H, CH), 7.80 (d, 2H, CH) and 8.20 (d, 2H, CH).

XRD Analysis

The XRD pattern show that in figure 1(a) pure CeO₂, having a cubic crystal structure of CeO₂ matches with JCPDS card No. 810792 [22] having parameter a=b=c= 5.412 Å. In the figure 1(b) the powder sample of Cs₂O having a hexagonal crystal structure of Cs₂O matches with JCPDS card no. 090104 [23] parameter are a=4.256, b=4.256, c=18.99 Å; α=β=90, γ=120. In the figure 1(c) the powder sample for CuO having a monoclinic crystal structure of CuO matches with JCPDS card no 800076, [24] the lattice parameter are a= 4.679, b= 3.431, c= 5.136 Å; α=β=γ=90.

The fig. 1(d) shows, XRD pattern of synthesized materials, which indicates decreases in intensity because of CuO and Cs₂O completely deposited on the surface of CeO₂. The plane (111) of CeO₂ matched with mixed metal oxide but more broadening of this peak is occurs due to decreases in particle size of CeO₂. The particle size can be calculated from Debye Scherer equation [25].

$$T = \frac{0.94\lambda}{\beta \cos\theta}$$

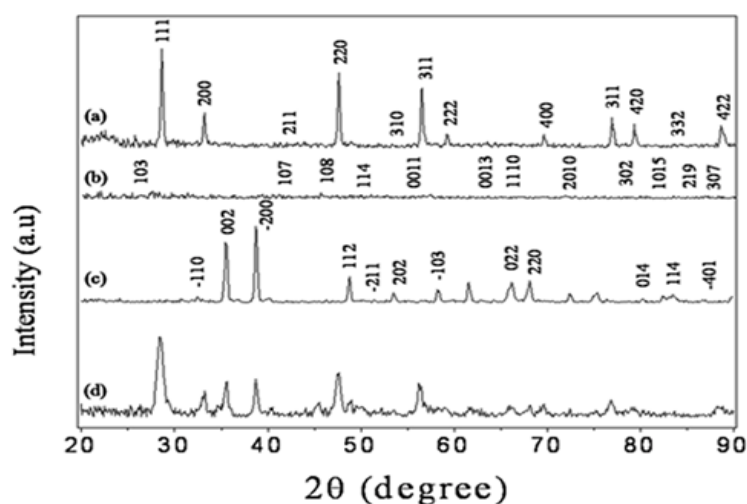


Figure 1 XRD pattern of a) CeO₂, b) Cs₂O, c) CuO, d) mixed metal oxide CeO₂-Cs₂O-CuO

Where, T is average particle size, λ is wavelength, θ is diffraction angle and β is FWHM (Full width half maximum). It observes that the particle size of pure CeO₂ is 30.94 nm, while smaller the size up to the 10.26 nm. Maximum peaks were matched for cubic structure of the CuO.

SEM-EDS analysis

The surface morphology of prepared catalyst was studied by SEM (Scanning Electron Microscopy) images. Fig. 2(a) shows the porous morphology of CeO₂, the Fig. 2(b) shows globular agglomeration morphology which is characteristic of Cs₂O. Fig. 2(c) shows rectangular morphology of CuO. A globular particle of Cs₂O gets absorbed into pores of CeO₂ and after that CuO gets adsorbed on this binary oxide, which helps in the formation of mesoporous material.

The FT-IR absorption bands, at 416 , 497 cm^{-1} and 540 cm^{-1} are observed (fig.4) due to presence of Cu and O bond. [26]. Because of O-H bending vibration the absorption band is observed at 1604 cm^{-1} [27] and 3433 cm^{-1} is observed from bridged O-H stretching vibrations. [28]

FT-IR analysis of Py-adsorption on catalyst

FT-IR techniques applied to identify surface acidity of catalyst, which was performed by adsorption of pyridine on catalyst surface. **Figure 5** (a) and (b) shows FT-IR spectrum, with and without pyridine adsorption, in **Figure 5** (b) the IR band around $1420\text{-}1450\text{ cm}^{-1}$ and $1630\text{-}1650\text{ cm}^{-1}$ are confirm the presence of Lewis and Bronsted acidic sites [29] which is contrast with **Figure 5** (a).

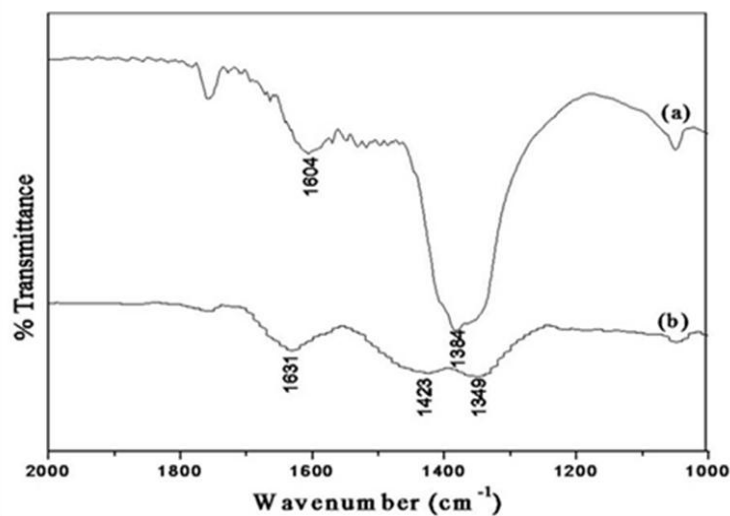


Figure 5 FT-IR spectrum of (a) without Pyridine Adsorption (b) Pyridine Adsorption on $\text{CeO}_2\text{-Cs}_2\text{O-CuO}$.

BET analysis

BET surface area has been determined by means of N_2 adsorption at 77 K by Quantachrome (CHEMBET 3000). It was found that BET specific surface area of catalyst $\text{CeO}_2\text{-Cs}_2\text{O-CuO}$ is $36.81\text{ m}^2/\text{g}$.

Conclusions

In summary, we have synthesized $\text{CeO}_2\text{-Cs}_2\text{O-CuO}$ inexpensive catalytic materials were successfully prepared by co-precipitation method using cetyl-trimethyl ammonium bromide (CTAB) as surfactant. Synthesized catalytic materials were characterized XRD, SEM-EDS, FT-IR, and BET to determine the structure and composition. After conformation, the catalyst synthesis of 9, 9, 10, 10 tetracyanonaphthoquinodimethane using naphthalene-1, 4-dione and, malononitrile. The present method offers several advantages properties such as shorter reaction time, simple experimental procedure, high yield of the products selectively.

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