Research Article

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Novel Azo-fused Dipyrazolopyridine Derivatives using Waste Orange Peel-derived C-SO_3H Nanopowder as an Efficient and Reusable Catalyst

N. Nagasundaram, S. Sumitha, A. Lalitha*
Department of Chemistry, Periyar University, Salem, TN, India
*lalitha2531@yahoo.co.in

ABSTRACT

A new series of structurally diverse azo-fused dipyrazolopyridines has been synthesized *via* one-pot pseudo-six-component reaction of various substituted aryl azo-salicylaldehydes with ethyl acetoacetate, hydrazine hydrate and ammonium acetate, using waste orange peel-derived carbon modified sulfonic acid (C-SO_3H) as a mild, efficient and inexpensive heterogeneous catalyst. The prepared catalyst was characterized by FT-IR, XRD, SEM, EDX and XPS studies. The catalytically synthesized compounds were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR. The notable advantage was the use of a recyclable powder catalyst (C-SO_3H) for excellent yields and rapid formation of the desired azo-fused dipyrazolopyridines with a simple work-up procedure.

Keywords: Dipyrazolopyridines; Greener catalyst; Solid acid catalyst; Waste orange peel.

1. INTRODUCTION

The utilization of solid heterogeneous catalysts delivers innovative methods in the field of green catalysis by enhancing efficiency, selectivity and effective role in the modern synthetic organic field (Kumar *et al.* 2014; Kandepi and Narender, 2012). In the recent scenario, the invention of new kind of carbon materials such as carbon nanotubes, carbon dots and ordered mesoporous carbons (Ryoo and Jun, 1999) is highly encouraging for the exploration of carbon particles because of their immense variety of applications like adsorbents, electrode materials, energy storage material, stationary phase in liquid chromatography and catalyst support. The utilization of bio-waste material-based carbon-modified solid catalysts is one of the attractive tools in the field of catalysis due to their inexpensiveness, eco-friendliness, high selectivity, ease of separation and reusability, compared to non-biomass-based catalysts. This work has been focused on the synthesis of novel azo-fused dipyrazolopyridine derivatives *via* a one-pot pseudo-six-component reaction using waste orange peel-derived carbon-modified sulfonic acid (C-SO_3H) catalyst.

2. RESULTS AND DISCUSSION

2.1 Characterization of prepared C-SO_3H catalyst:

FT-IR analysis

The broad vibration band at 3415 cm^{-1} has indicated the –OH stretching vibrations of sulfonic acid moieties; the bands at 1636 cm^{-1} and 1029 cm^{-1} represented the presence of asymmetric and symmetrical stretching modes of SO_2, showing the presence of sulfonic acid groups in OPC-SO_3H material. In the powder X-ray diffractogram, a broad peak at the diffraction mode of $2\theta = 25^{\circ}$ can be attributed to the amorphous nature of the prepared OPC-SO_3H material.

SEM

SEM images have indicated that the prepared catalyst was in agglomerated structure. EDAX spectrum has shown the elemental composition of the C-SO_3H (Carbon = 54.39%, Oxygen = 38.36% and Sulfur = 7.25%). XPS spectrum has shown the binding energy of elements presented on the surface of C-SO_3H (Carbon = 283.6 eV, Sulfur = 168.35 eV and Oxygen = 531.15 eV).

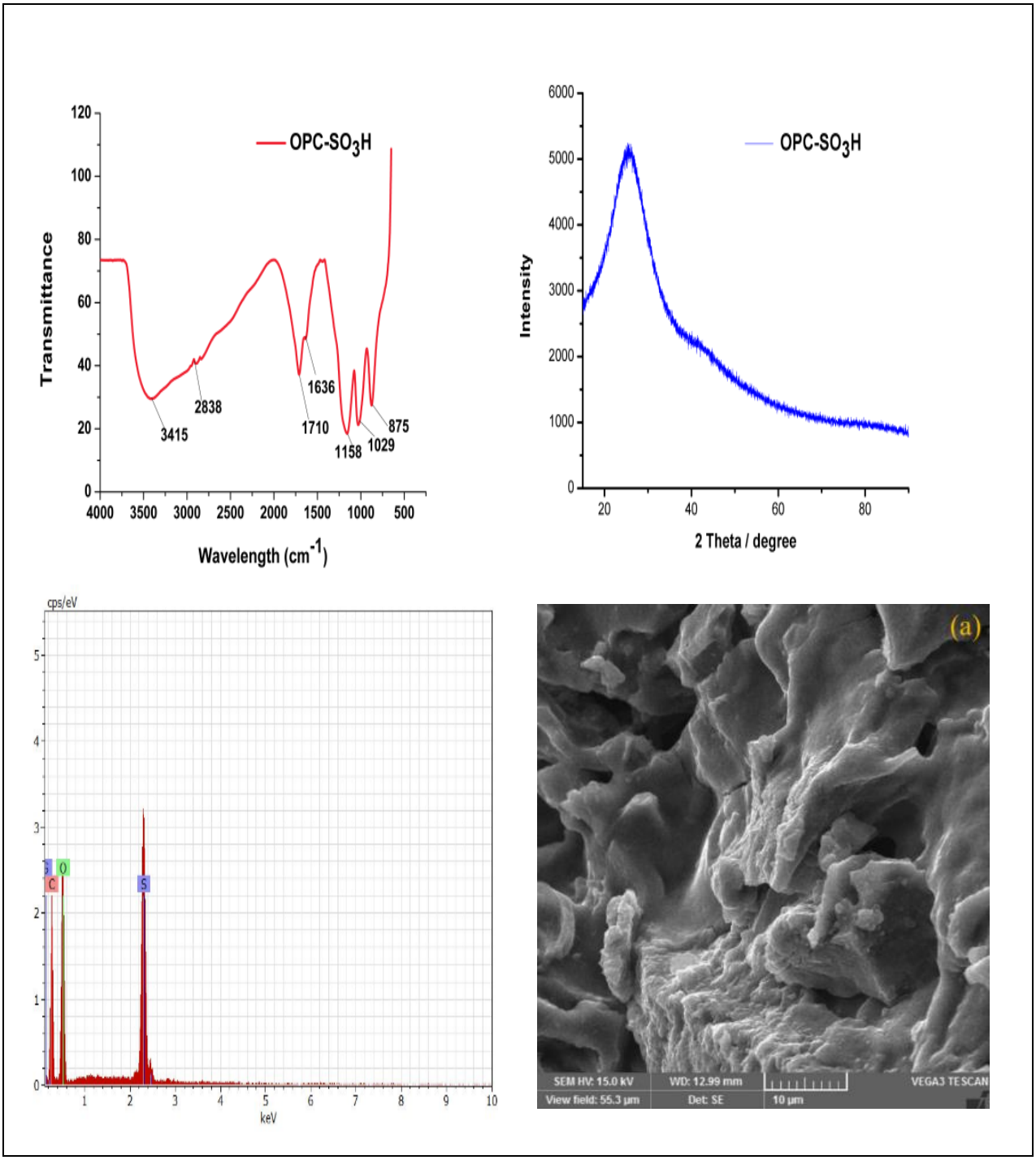
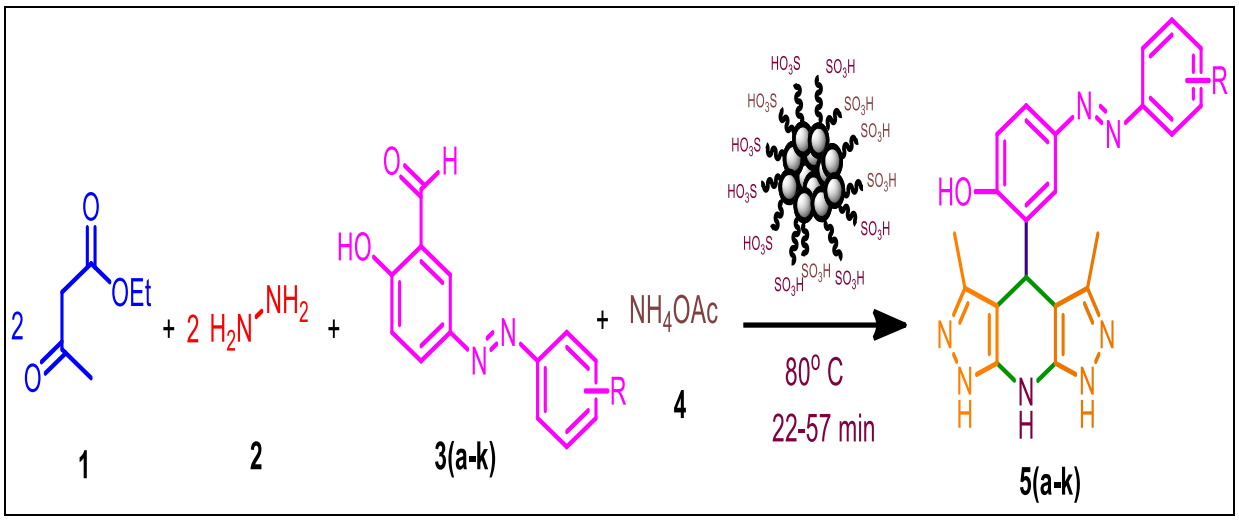


Fig. 1: Characterization of C-SO_3H material: (a) FT-IR (b) XRD (c) SEM (d) EDAX (e) XPS.

2.2 Catalytic activity

An attempt has been made to explore the catalyst efficacy of OPC-SO_3H nano-powder by experimentation with pseudo-six-component reaction of ethyl acetoacetate 1 (2.0 mmol), hydrazine hydrate 2 (2.0 mmol), various substituted aryl azo salicyclaldehydes 3 a-k (2.0 mmol) and ammonium acetate 4 (2.0 mmol), using 20 mg of C-SO_3H catalyst in ethanol solvent at refluxing temperature leading to the formation of novel tetrahydrodipyrazolopyridin-4-yl) -4-(phenyldiazenyl) phenol (5 a-k). In addition, the reaction conditions have been optimized using various solvents and temperatures for obtaining better reaction time and targeted yields.



Scheme 1. Synthesis of novel Azo-fused tetrahydrodipyrazolo-4yl)-4-(aryldiazenyl) phenol derivatives using C-SO_3H catalyst

Entry	Aldehyde	Product	Time (min)	Yield (%)	Melting point (°C)
1	H	5a	24	90	Above 300
2	4-Cl	5b	22	92	218-220
3	3-Cl	5c	27	87	Above 300
4	2-Cl	5d	22	90	294-296
5	4-F	5e	25	85	Above 300
6	4-Br	5f	29	92	220-222
7	4-NO_2	5g	37	86	Above 300
8	3-NO_2	5h	26	90	254-256
9	4-OCH_3	5i	27	89	Above 300
10	4-CH_3	5j	39	92	Above 300

Scheme 2. Reaction conditions of: Ethyl acetoacetate (4.0 mmol), Hydrazine hydrate (4.0 mmol), Ammonium acetate (4.0 mmol) and various substituted 5-aryl azo salicylaldehyde (2.0 mmol) with C-SO_3H (20 mg), at 80 °C isolated yields.

3. CONCLUSION

In summary, a C-SO_3H powder catalyst was designed and developed *via* simple pyrolysis followed by a sulfonation process. It was utilized as a greener, inexpensive heterogeneous catalyst for the synthesis of novel azo-fused dipyrazolopyridine derivatives *via* a one-pot pseudo-six-component reaction. The prepared catalyst was reused up to 7 cycles without loss of its activity; it was found to be environment-friendly.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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