

A GREEN APPROACH FOR THE CONVERSION OF
2,3-DIHYDRO-2-PHENYL-4-QUINOLONE TO 2-PHENYL-4-QUINOLONE USING
INDUSTRIAL WASTE COAL FLY ASH SYNTHESIZED MCM-41.

Pande G.B¹, Deshpande M.R² And Shirodkar S.G.³

¹Department of Physics, Netaji Subhashchandra Bose College, Nanded.(M.S.)

²Department of Chemistry, Netaji Subhashchandra Bose College, Nanded.(M.S.) ³Department of Physics, Netaji Subhashchandra Bose College, Nanded.(M.S.)

ABSTRACT

As an alternative reagent to various traditional dehydrogenating reagents CFA-Si-MCM-41 is stable, non-hazardous, acidic and has been successfully used for dehydrogenation reactions. Herein we report a new and ecofriendly route for dehydrogenation of 2,3-dihydro-2-phenyl-4-quinolone to 2-phenyl-4-quinolone using CFA-Si-MCM-41 and 2 potassium hydroxide. A series of 2,3-dihydro-2-phenyl-4-quinolones has been synthesized using acid-catalyzed one-pot reaction. Quinolones were prepared through cyclization of the condensation product that were formed by heating of arylamines and ethyl benzoylacetate in toluene. Similarly, the 6 (7 or 8)-substituted 2,3-dihydro-2-phenylquinolones were prepared from the para (ortho or meta)-substituted aniline.

Keywords: CFA-Si-MCM-41, 2,3-dihydro-2-phenyl-4-quinolone, 2-phenyl-4-quinolone.

INTRODUCTION

The entire industries all through the human planet turn out a harmful dissipates like agricultural wastes, electronic wastes, toxic chemical wastes, biological wastes, industrial wastes etc creating major challenges such as serious health risks and environmental problems¹⁻⁷. Several chemicals for instance HF, H₂SO₄,

HClO₄ and H₃PO₄ are used primarily in the areas of oil refining, petrochemicals and so on, but they have many disadvantages like difficulties in handling, plant corrosion, revival and environmentally safe disposal.

Many of the substances, such as cadmium, arsenic, chromium, nickel and dioxins are considered to be carcinogenic which causes cancer, effects on the central nervous system, liver, kidneys, heart, lungs, skin, reproduction and many others.

Likewise, in electric power generating plants, Coal fly ash is a byproduct from burning pulverized coal. During combustion, mineral impurities in the coal (clay, feldspar, quartz, and shale) fuse in suspension and float out of the combustion chamber with the exhaust gases. As the fused material rises, it cools and solidifies into spherical glassy particles called as fly ash. These fly ash particles create serious ecological problems and also disposal of such a massive quantity of ash has become a vital issue⁸⁻¹⁰. The disposal of coal fly ash from coal based power plants is a problem of global concern today. In India most of the utility is thermal power and sub-bituminous coal with high ash content of 35%-60% resulting in the production of a huge quantity of fly ash.

In India, a little effort has been paid on proper utilization of fly ash. A very small quantum (3%) of huge quantity of fly ash is used as a raw material for concrete manufacturing and construction purpose, in asbestos sheets, in road reclamation and

agriculture purpose, while remaining is being unfortunately dumped on the landfill sites. Presently, more than 90 mt (million tons) of fly-ash is being generated in India, with more than 70000 hectares of land being occupied by ash ponds which posed a great threat to the environment.

Coal Fly ash (CFA) is the low cost and readily available silica rich raw material which can be used for the preparation of value added porous materials like zeolite molecular sieves¹¹. Converting fly ash into zeolites not only eliminates the disposal problems, but also turns an otherwise waste material into a marketable commodity as they have widespread applications in diversified fields.

The major components of CFA are silicon dioxide (SiO₂) and Aluminium trioxide (Al₂O₃), which are the essential reagents in the synthesis of zeolites (Shigemoto et.al., 1993; Chang and Shish, 1998). Synthetic zeolites obtained by reprocessing of CFA have huge potential as a cost-effective, environmentally-friendly solution that can improve the competence of these materials as efficient heterogeneous catalysts, mainly as solid acids, as adsorbents, as molecular sieves in gas separation and purification¹²⁻¹⁴ and in purification of contaminated waste water^{15,16}. The low price and the additional ecological benefit of the production of zeolites from wastes increased their popularity and inspired growing interest among zeolite researchers and manufacturers worldwide.

According to IUPAC¹⁷ definitions zeolitic porous materials may be divided into three categories based on their pore magnitudes as shown in Table 1.

Pore Size (nm)

Microporous : < 200 Mesoporous : < 200-5000 Macroporous : > 5000

'Zeolites' the aluminosilicate molecular sieves¹¹ are microporous materials which are inorganic composites. They have a crystalline structure woven with tetrahedral atoms like Al, P, Si etc bridged by oxygen atoms acquiring regular channels or cavities with an explicit number of tetrahedral atoms¹⁹⁻²². The crystallographic unit cells of the zeolites may be represented as: $M_{x/n} [(AlO_2)_x (SiO_2)_y] zH_2O$

Where,

M is a charge compensating cation with valency 'n'. The ratio 'x/y' may have any value ranging from zero to one. The number of water molecules, which can be reversibly adsorbed and desorbed in the zeolite pores, is represented by 'z'. Total number of tetrahedral sites in the unit cell of zeolites represented by x + y. In general, the ratio (y/x > 1) controls the morphology of zeolites and acidity to a lesser extent.

The presence of trivalent Al atoms in the lattice develops a unit negative charge per Al atom in the framework, which is compensated by a cation such as proton (H⁺) producing acidity in zeolites. A significant breakthrough in zeolite science occurred in 1982 when Wilson and co-workers²³ disclosed the synthesis of a novel crystalline, microporous aluminophosphate (AlPO₄) materials with pores formed by more than 12 tetrahedral atoms about 0.8 nm in diameter. Later, in 1988, Davis et. al.²⁴, reported the synthesis of VPI-5, an AlPO₄ molecular sieve with 18 tetrahedral atom rings that could sorb molecule about 1.3 nm in size.

In 1992, researchers at Mobil Research and Development Corporation reported the synthesis of a new family of silicate/aluminosilicate mesoporous molecular sieves (M41S) with exceptionally large and uniform pore structures.²⁵⁻²⁷ These materials possess well-

defined mesopores whose diameters can be tailored in the range of 20Å-100Å with high surface area (>900m²/g) and precise tuning of the pores are among the desirable properties of these materials. Mainly these materials used in a new synthetic approach where, instead of a single molecule as templating agent as in the case of zeolites, self-assembly of molecular aggregates or supramolecular assemblies are employed as templating agent (surfactant molecules). Which are large organic molecules having a long hydrophobic tail of variable length (e.g. alkyltrimethylammonium cations with formula C_nH_{n+1}(CH₃)₃N⁺, where n > 8) and a hydrophilic head. Among the M41S materials, the hexagonally channel oriented MCM-41 received much attention than the others because of their better thermal stability, large surface area and narrow pore size distribution. MCM-41 is structurally stable towards thermal treatment, hydrothermal treatment with steam at mild conditions, mechanical grinding and also towards acid treatment at mild condition. MCM-41 has high potential for practical use as an adsorbent or a mesoporous support for depositing active catalyst components, particularly useful in the synthesis of fine chemicals involving bulky molecules.

The large regular pore structure of MCM-41 materials make them suitable for liquid-phase acidic and basic catalysis by enabling rapid diffusion of reactants and products through the pores, thus minimizing consecutive reactions. Liquid-phase Friedel–Crafts alkylation and the acetalisation of bulky aldehydes, Knoevenagel condensations etc. have been reported using MCM-41.

PRE TREATMENT ON CFA AND RICE HUSK

CFA obtained from Chandrapur and Parali TPS, was initially screened through a BSS Tyler sieve of 80-mesh size to eradicate the larger particles. The unburnt carbon along with other volatile materials present in CFA was removed by calcination at 800°C for 5h in muffle furnace. CFA was then treated with dilute hydrochloric acid to remove iron to a certain extent, thereby increasing the activity and thermal stability of the synthesized material all aiming for better catalytic and adsorptive applications. An amorphous SiO₂ component in the CFA was used as Si-source for the further investigations.

CHEMICAL COMPOSITION OF COAL FLY ASH (CFA) AND RICE HUSK ASH (RHA)

X-ray fluorescence (XRF) was used to determine chemical compositions of the fly ash. Fly ash is mainly composed of some oxides derived from inorganic compounds, which remain even after the combustion of coal. The amounts of the main components of ash viz. both amorphous (mainly SiO₂, Al₂O₃) and crystalline components (mainly quartz and mullite) show few variations with the type of coal. The Chemical composition of fly ash collected from Chandrapur and Parali (vz) TPS used in the present study are given in Tables 1. From the chemical analysis of CFA obtained from Chandrapur TPS and Parali TPS, we came to know that CFA of Chandrapur TPS is more silicious, therefore we have decided to take it as a main Silica source instead of CFA of Parali TPS.

SYNTHESIS OF MESOPOROUS MCM-41 FROM CFA IN ALKALINE MEDIUM

Mixture of sodium hydroxide and CFA (calcined and HCl treated as in 2.2.2) in a pre-determined ratio i.e. 30gm CFA fused with NaOH solution (1M, 2M, 3M) was stirred in a

hydrothermal reactor Fig.2. at different temperatures (Room temperature to 1600C) for 4 hrs under stirring condition (300 rpm). The mixture was filtered after cooling. The filtered liquid is an extracted silica gel and was referred as solution A (Supernatant). Further 1.1 gm of cetyltrimethyl ammonium bromide (CTAB) was dissolved in few quantity of deionized water. This is referred as solution B (Surfactant).

The supernatant (90ml) and surfactant (solutions A and B) were blended together drop by drop and were kept under stirring (300 rpm) at 850C for crystallization. After 30min, 3ml Ethyl acetate as a mild acid hydrolyser was vigorously mixed and the solution was kept under stirring at 600 rpm for next 20min. The molar composition of the synthesis gel was as follows:

1.0SiO₂: 1.5NaOH: 0.008 (CTAB): 0.08 EA: 42H₂O.

The obtained solution was then allowed to cool to room temperature by natural convection and was adjusted to the selected pH (1.87, 3.32, 4.72, 5.73, 6.25, 6.91, 8.56, 10.12 and 11.20) by adding 5.25N H₂SO₄ solution bit by bit under slow stirring. After the crystallization, the product was filtered. Precipitate obtained during pH adjustment was kept at room temperature for 18 hrs.

The white solid cake obtained after filtration was frequently washed by deionized water and dried at 1000C for 2 hrs. This dried material was calcined under air at different calcination temperatures (5000C to 8000C) at a ramp of 500C at a heating rate of 10C/min for different durations of calcinations (1.5h-12h). After cooling, the samples were characterized for the investigation of optimization. This synthesized material is further known as CFA-Si-MCM-41.

CHARACTERIZATIONS

Every natural or synthetic material (viz. zeolites and other solid porous materials) need to be completely characterized by a number of physical, chemical and spectroscopic techniques to elucidate their structural features, morphology, pore architecture, thermal stability, adsorptive and catalytic behavior, surface area etc. Synthesized samples are characterized by techniques such as XRD, N₂- sorption, SEM, TGA/DTA, FTIR, NH₃ and CO₂-temperature programmed desorption, etc. Among these, X-ray diffraction is of primary importance which provides information on the phase purity and some evidence for heteroatom incorporation. The sorption capacity data provide surface area, pore volume and pore size. SEM is an established technique to obtain the morphological information.

All the characterization techniques performed in this study reveals that well-ordered mesoporous material of uniform hexagonal array can be synthesized very conveniently and in a very short span of time from an agricultural waste rice husk ash. Even after their post modification, no marginal changes are found in their structural morphology i.e. the structure of CFA-Si-MCM- 41 remained more intact. Hence, these modified forms may be used in basic or acidic catalytic reactions.

Quinolones²⁸ are analogues of flavanones and thiaflavanones which are characterized by a fused benzoring and phenyl substituent. Quinolones are broad-spectrum antibiotics that play an important role in treatment of serious bacterial infections, especially hospital-acquired infections and others in which resistance to older antibacterial classes is suspected. Quinolones are bactericidal agents that target the bacterial DNA gyrase enzyme. Many

quinolones have pharmacodynamic properties that result in high intracellular concentrations in host inflammatory cells.

RESULT AND DISCUSSION

A series of novel substituted 2,3-dihydro-2-phenyl-4-quinolones were prepared by cyclisation of substituted 1-(2'-aminophenyl)-3-phenyl-2-propene-1-one by using ZnCl₂. Substituted 2,3-dihydro-2-phenyl-4-quinolones were dehydrogenated using CFA-Si-MCM-41 in 0.1 N KOH.

EXPERIMENTAL

All the chemicals used were of S.D. Fine chemicals. All the solvent used were distilled previously. Clay was purchased from Aldrich chemicals. Melting points were measured in open glass capillaries on a Perfit Electro-thermal melting-point²⁹ apparatus and are uncorrected. H NMR spectra were recorded at room temperature on a 300 MHz. Varian Inova Spectrometer in CDCl₃ using TMS as internal standard level for all the experiments. The reactions were monitored by TLC using pre-coated plates (Merck).

A solution of substituted 1-(2'-aminophenyl)-3-phenyl-2-propene-1-one (3.0 m moles) and Zinc chloride (1 M in Et O, 3.3 m mole) in CH₃CN (12 ml) was heated to 80°C for (24 hrs) after evaporation of 2/3 CH₃CN the mixture was poured into saturated solution of NH₄Cl (30 ml) and extracted with methylene chloride (3 x 20 ml).

Preparation of 2,3-dihydro-2-phenyl-4-quinolone:

GENERAL PROCEDURE

Dehydrogenation of 2,3-dihydro-2-phenyl-4-quinolone to 2-phenyl-4-quinolone :

To compound 5 (2 m.mole) was added a solution of 0.1 N KOH in CH₃OH (60 ml 6 m. mole) and CFA-Si-MCM-41 (7.09 mg 2.2 m mole) at room temperature. The mixture was heated to 60°C for 16 hrs. After evaporation of CH₃OH, 0.05 N HCl (50 ml) was slowly added to the mixture at 0°C. The resulting precipitate was separated by filtration washed with H₂O and re-crystallized by CH₃OH.

SPECTRAL ANALYSIS

The structures of the products were confirmed from NMR, IR and LCMS^{30,31}. The representative spectral analysis for few of the products is given below. The observed values are in accordance with the literature values as depicted in table 2.

Compound - I :

PMR : 4.0 (1H,s), 7.21(5H,m), 4.44(1H,t), 3.07 (2H,d), 7.55 (1H,d), 6.60 (1H,dd), 7.23 (1H,d). IR :

3432 (NH), 3064, 2964, 1632 (C=O, C=C), 1580, 1546, 1504, 1472, 1450, 1432, 1256, 1140, 770 cm.

Compound – II:

PMR :4.0 (1H,s), 7.18 (5H,m), 4.40 (1H,t), 3.02 (2H,d) 7.61 (1H,d) 6.55 (1H,dd) 7.39 (1H,d). IR :

3430 (NH), 3068, 2960, 1630 (C=O, C=C), 1580, 1546, 1500, 1470, 1452, 1432, 1142, 768 cm.

Compound – III:

PMR :4.02 (1H,s), 7.20 (5H,m), 4.42 (1H,t), 3.04 (2H,d), 7.66 (1H,d), 6.43 (1H,dd), 7.60 (1H,d). IR :

3436 (NH), 3065, 2963, 1628 (C=O, C=C), 1578, 1540, 1502, 1474, 1455, 1432, 1250, 1140, 766 cm.

Compound – IV:

PMR :4.04 (1H,s), 7.16 (5H,m), 4.40 (1H,t), 3.05 (2H,d), 7.39 (1H,d), 6.66 (1H,dd), 6.98 (1H,d). IR :

3436 (NH), 3068, 2966, 1636 (C=O, C=C), 1588, 1548, 1508, 1478, 1458, 1436 1255, 1140, 772cm.

Compound – V:

PMR : 4.02 (1H,s), 7.12 (5H,m), 4.40 (1H,t), 3.06 (2H,d), 7.52 (1H,s), 7.20(1H,s). IR: 3436 (NH),

3068 2960, 1630 (C = O, C = C), 1588, 1548, 1506, 1470, 1448, 1436, 1258, 772 cm.

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