Praise Worthy Prize

International Review of Chemical Engineering (I.RE.CH.E.), Vol. 4, N. 6
ISSN 2035-1755 *November 2012*
Special Section on 4th CEAM 2012 - Virtual Forum

A Facile Solvent-Free Skraup Cyclization Reaction for Synthesis of 2, 2, 4-trimethyl-1, 2-dihydroquinoline

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Abstract – *An optimized and efficient process has been found to synthesize 2, 2, 4-Trimethyl-1, 2-dihydroquinoline from an acid- catalyzed Skraup Cyclization of acetone and aniline. Polyhedral oligomeric silsesquioxane functionalized with sulfonic acid group [POSS-SO3H] used as an acid catalyst, synthesized by self-assembly of silane precursor was used. Different characterization of POSS-SO3H using TPD, SEM, XRD, TGA and FT-IR was carried out. The comparative study of the effect of reaction parameters such as speed of agitation, mole ratio, catalyst loading and temperature was analyzed to obtain maximum conversion.* ***Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.***

Keywords: *Solid Acid Catalyst, POSS, Skraup Cyclization, 2, 2, 4-Trimethyl-1, 2-Dihydroquinoline, Langmuir-Hinshelwood-Hougen-Watson Mechanism*

Nomenclature

A	Acetone
B	Aniline
C	2, 2, 4-Trimethyl-1, 2-dihydroquinoline
C_A	Concentration of acetone (mol/cm^3)
C_B	Concentration of aniline (mol/cm^3)
C_C	Concentration of 2, 2, 4-Trimethyl-1, 2-dihydroquinoline (mol/cm^3)
C_s	Concentration of vacant sites (mol/ g catalyst)
C_t	Total concentration of sites (mol/ g catalyst)
C_W	Concentration of water (mol/cm^3)
E_a	Activation energy (kcal/mol)
K	Forward rate constant for cyclization reaction
k	Effective rate constant for cyclization reaction
K'	Backward rate constant for cyclization reaction
K_A	Adsorption equilibrium constant for A
K_B	Adsorption equilibrium constant for B
K_C	Adsorption equilibrium constant for C
K_W	Adsorption equilibrium constant for W
M	Molar ratio of acetone to aniline
r_A	Rate of reaction w. r. t. A (mol/cm^3 min g catalyst)
W	Water
w	Catalyst loading (g/cm^3)
X	Fractional conversion

I. Introduction

The increasing chemical pollution in the recent decades has escalated the demand for extensive and effective implementation of green chemistry. Catalysis plays a pivotal role in green chemistry and waste minimization [1]. The synthesis of dihydroquinolines and their derivatives have been the focus of prolonged interest among organic and medicinal chemists for many years due to its widespread availability and enhanced biological activity [2]-[4]. Many derivatives of 2,2,4-trisubstituted-1,2-dihydroquinolines are known to exhibit a wide range of pharmacological properties such as bactericidal[5], anti-diabetic[6], anti-inflammatory[7], anti-malarial[8], lipid per-oxidation inhibitors[9], progesterone-agonists[10] and antagonists[11]. Furthermore, the utility of 2, 2, 4-trimethyl-1, 2-dihydroquinolines as antioxidants for rubber and poly-olefins, feed additives, dyes, and pharmaceuticals is also well-recognized [12]-[19]. Its polymeric form i.e. Rubber Anti-oxidant RD is mainly used for natural rubber and chloroprene rubber etc. It has stronger restrained effect to the metallic catalysis and oxidation. It has a longer-time remaining of protective effect, because it has a higher molecular weight and has little diffusive loss [20].

Silica [21] is commonly used as a catalyst support since it can withstand extensive 3D network structures. One class of silicones is silsesquioxanes [22] i.e. silicones with a Si: O ratio of 1:1.5. These structures are called polyhedral oligomeric silsesquioxanes or POSS with a general formula of $[RSiO_{1.5}]_n$ (see Fig. 1). Polyhedral oligomeric silsesquioxanes (POSS) are thermally robust cages consisting of a silicon–oxygen core framework possessing alkyl functionality on the periphery [22]-[29]; they are used for the development of high performance materials in medical, aerospace, and commercial applications [30]. POSS molecules can be functionally tuned, are easily synthesized with inherent functionality, are discreetly nano-sized, and are often commercially available.

In this system, POSS crystals have been effectively synthesized by the process of self-assembly. Functionalization of POSS [31]-[35] was carried out so as to impregnate acidic sites, and was then characterized by several techniques including Temperature

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Programmable Desorption (TPD), X-Ray Diffraction (XRD), Fourier Transform Infrared (FT-IR) Spectroscopy, Thermo Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM).

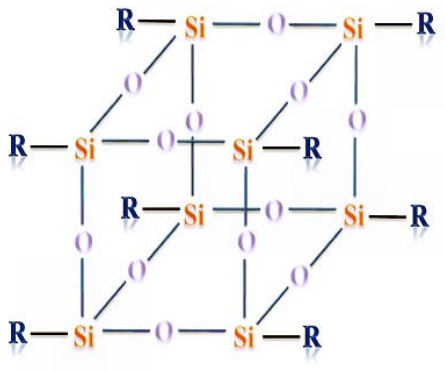

Fig. 1. Basic structure of POSS, R-hydrogen/alkyl/alkylene/aryl/arylene

Among the most general approaches for the synthesis of such dihydroquinolines is Skraup cyclization which involves the heating a mixture of nitro-ethane, aniline, and glycerol with concentrated sulfuric acid [36]. Doebner and Von Miller modified this procedure by using an alpha and beta unsaturated ketone with an aromatic amine by heating in the presence of acid catalyst or iodine [37]. Over the last century, a number of other methods have been made to improve the yields and reproducibility of Skraup cyclization involving a variety of catalysts [38]. However, in spite of the potential utility, some of these methods suffer from drawbacks including the use of unavailable and costly reagents, higher temperature, longer reaction times, lower yields and the use of hazardous solvents. Another important issue is that most of these procedures involve either conventional heating or microwave-irradiation

On studying the various solvent-free reactions, [39]-[45], we would like to put forward a POSS-SO3H acid-catalysed reaction for the synthesis of 2, 2, 4-trisubstituted-1, 2-dihydroquinolines at different temperature under solvent-free conditions. It involves the formation of a self-aldol condensation product which attacks aniline to form the desired quinoline. In this study, the reaction kinetics of POSS-SO3H catalyzed Skraup cyclization reaction (Fig. 1) of aniline with propan-2-one has been examined to synthesize 2, 2, 4-trimethyll-1, 2 di-hydroquinoline.

II. Experimental

II.1. Materials

3-mercaptoproyl trimethoxy silane (3-MPTS) precursor were obtained from Fluka, USA; sulfuric acid, hydrogen peroxide, methanol, ethanol, aniline, acetone , toluene, n-dodecane, aqueous ammonia solution, were obtained from M/s. S. D. Fine Chemicals, Mumbai, India and use of analytical grade.

II.2. Catalyst Preparation

II.2.1. Synthesis of mercaptopropyl polyhedral oligomeric silsesquioxane (POSS-SH)

Silane precursor (3-mercaptopropyl trimethoxy silane) was hydrolyzed using aqueous ammonia solution which performs as a catalyst, in the presence of ethanol as solvent. The reaction mixture was stirred at room temperature (30^{o}C) for 48 h [23]. Initially, the reaction concoction was transparent indicating complete dissolution of silane monomers. After 2 hours of the reaction as the hydrolysis and condensation reaction proceeded, the mixture became opaque indicating the formation of colloidal particles. The product started to precipitate from the suspension in duration of stirring. Finally, the reaction concoction with almost clear supernatant was obtained after 48 hour. The precipitate obtained was filtered, washed and dried in an oven for 4 h at 60^{o}C.

II.2.2. Oxidation of POSS-SH to sulfonic acid POSS (POSS-SO_3H)

Excess amount of 30% hydrogen peroxide solution, required for complete oxidation were added to the precipitate with methanol as solvent, stirred in a magnetic stirrer for 4 h [46]-[50]. The final product was filter out using methanol solvent and dried. In order to ensure that all the sulfonic groups were protonated, the solid was suspended in a 10 wt% H_2SO_4 (~100 ml) solution for 1 h. The solid was then filtered off and washed with water and it was then dried in an oven for 4 at 60^{o}C.

II.3. Catalyst Characterization

For characterization of catalyst, the Fourier Transform Infrared (FT-IR) Spectroscopy was done on Perkin Elmer Spectrum GX, in the scan range of 4000 cm^{-1} and 600 cm^{-1}. XRD was obtained by a Rigaku Miniflex X-Ray Diffractometer and was used to confirm the crystalline structure. Thermal stability was determined by DSC-TGA using a Perkin Elmer Pyris Diamond TG/DTA. The surface morphology was studied by using JEOL JSM 6380LA analytical Scanning Electron Microscopy (SEM) and elemental analysis was done by using Energy Dispersive X-ray Spectroscopy (EDXS) (JEOL JSM 6380LA Analytical scanning Microscope). To determine the acidic/basic character, Temperature Programmable Desorption (TPD) was done on a Micromeritics 2920 TPD/TPR Analyzer

II.4. Reaction Procedure

The reaction as depicted in the scheme 1 was carried out at different reaction conditions in a laboratory autoclave. The reaction parameters were optimized to determine the optimum speed of agitation, molar ratio of reactants, catalyst loading and temperature.

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II.5. Method of Analysis

The analysis was carried out by GC (Chemito model 1000, FID detector) using a BPX50 capillary column (0.22 mm ×30 m). The product conformation was done by using GC–MS (QP2010 GCMS, Shimadzu restek, phase: Rtxwax, length 30 m, 0.25 mm I.D., 0.25 µm).

III. Result and Discussion

III.1. Catalyst Characterization

III.1.1. Fourier Transform Infrared (FT-IR) Spectroscopy

Qualitative identification of the organic functional groups in the materials was performed by FTIR spectroscopy. IR spectra of the silane monomer and silane-based cubic crystals, two peaks at 2942 and 2927 cm^{-1} are observed (see Fig. 2), which can be assigned to C–H stretching vibrations from propyl and methoxy groups in the silane monomer, respectively.

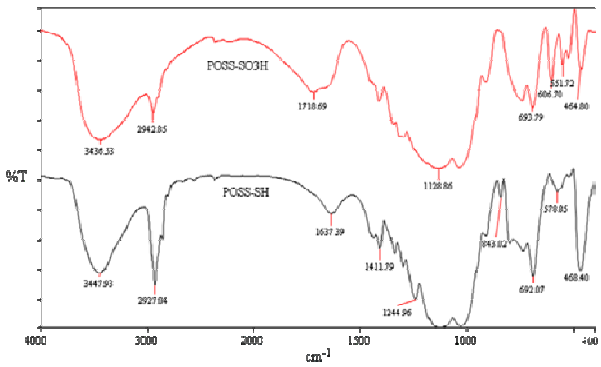

Fig. 2. FT-IR spectra before (POSS-SH) and after functionalization (POSS-SO_3H)

For mercaptopropyl-trimethoxysilane-based cubic crystals, the asymmetric Si–O–Si stretching vibration bands were observed at 1128 cm^{-1} [51]-[53]. For a random network structure, the Si–O–Si absorption peak usually appears around 1050 to 1000 cm^{-1}. More evidence for the cage structure of cubic crystals is the existence of a symmetric Si–O–Si stretching vibration peak at 551 cm^{-1}, which is the characteristic feature of a double ring from the cage structure [51]. In addition, peaks at 693 cm^{-1} and 843 cm^{-1} can be assigned to Si–C stretching vibrational and Si–$(CH_2)_3$ rocking modes, respectively [51]-[53]. The spectrum clearly shows the symmetric stretching's of Si–O–Si peak at ~770–1100 cm^{-1} which corresponds to the silsesquioxane cage structure [54]-[59]. The small peak at 2942 cm^{-1} can be attributed to the [(C–H)] deformation mode [60]. The wide and strong band at ~3450 cm^{-1} is assigned to the OH deformation due to H_2O.

III.1.2. X-ray Diffraction (XRD)

Powder X-ray diffraction analyses were performed on all the MPTMS-functionalized materials. The samples without pore directing agent showed no reflection peaks, indicating (see Fig. 3) no long range ordering of the mesopores in these materials by the template-free route. This is in contrast to functionalized SBA- 15 samples, which have one intense peak and two weak peaks, indexed to diffractions, characteristic of materials with ordered hexagonal arrays of one dimensional channel structure [61].

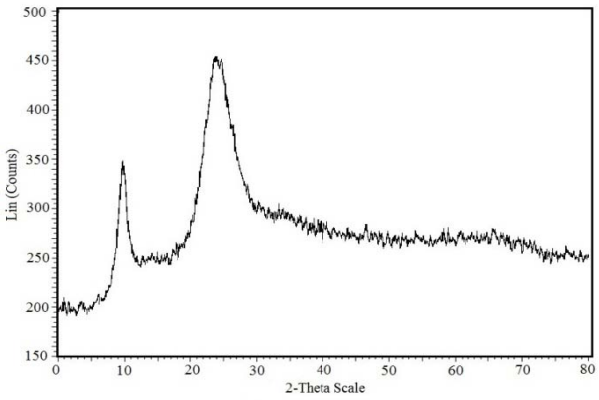

Fig. 3. XRD result after functionalization (POSS-SO_3H)

XRD pattern showed sharp crystalline peaks at 2θ =10° and 25°, which are in close agreement with the literature results for POSS structures [62]-[65] The resulting crystalline and amorphous phases in the synthesize materials are denoted as sulfonic acid-functionalized partially crystalline POSS material [66]. The X-ray powder pattern of POSS shows two main characteristic diffraction peaks at 10^o and 25^o (2θ), the peaks at 10^o (2θ), is for the size of POSS molecule.

III.1.3. Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) revealed that the catalyst was thermally stable up to a temperature of 250°C, and the overlay of the plots before and after functionalization indicates (see Fig. 4) the addition of oxygen atoms due to a reduction in the thermal stability.

It is reasonable to conclude that the crystallinity of pseudo cubic powders is slightly lower than that of cubic crystals [65]-[66]. The TGA curve for the spherical particles from the sol–gel process shows a quite different decomposition behavior. The sublimed cubic crystals lost their cubic morphologies resulting in amorphous powder-like materials.

III.1.4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDXS)

Scanning Electron Microscopy (SEM) divulge the SEM images of sulfonic acid functionalized POSS materials, presence of regular cubic shaped crystals after functionalization, whereas before functionalization globular aggregates were present (see Figs. 5).

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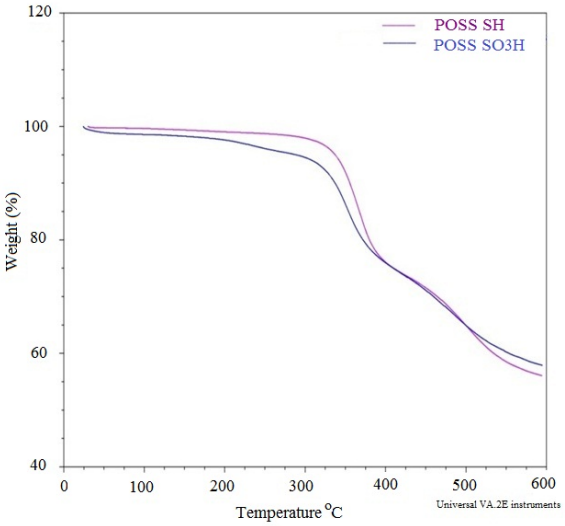
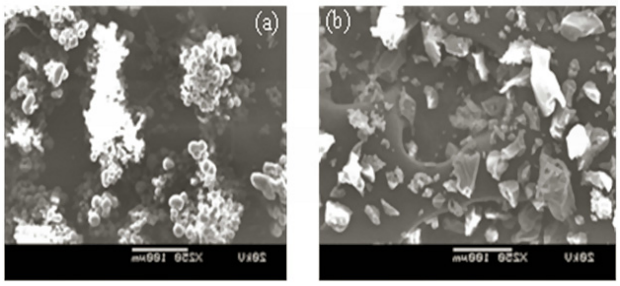


Fig. 4. XRD result after functionalization (POSS-SO_3H)



Figs. 5. SEM images before (a) and after functionalization (b) of POSS

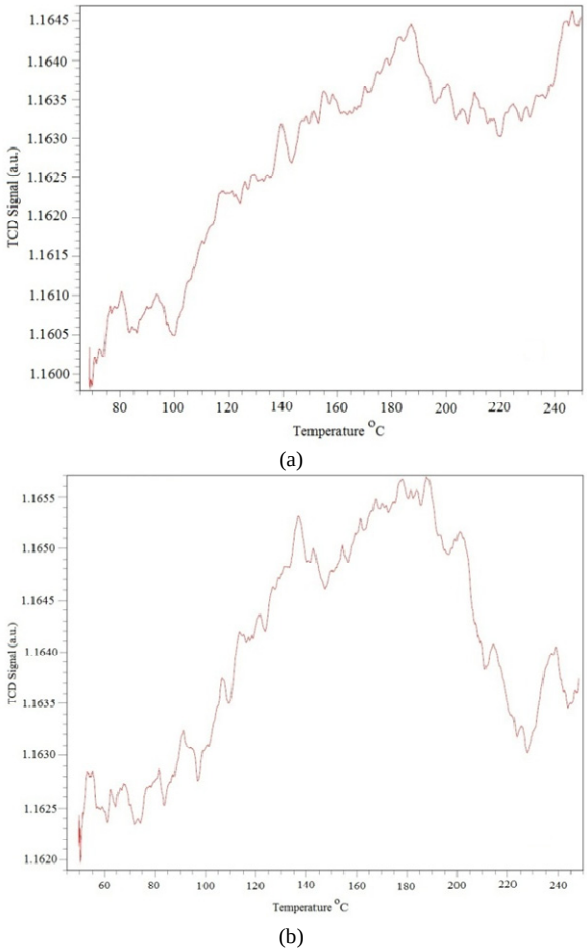
EDXS was done to confirm composition of sulphur, silicon and oxygen in synthesized catalyst. Table I shows sulfur (S), Silicon (Si) and Oxygen (O) contents in the sulfonic acid-functionalized POSS samples obtained from elemental analysis. The amount of S, Si and O present in the un-functionalized POSS samples was relatively low as compared to functionalized POSS

TABLE I
ELEMENTAL COMPOSITION

Element	Composition%	
	Before functionalization	After functionalization
O	21.47	48.45
Si	45.66	35.63
S	32.87	15.92

III.1.5. Temperature Programmed Desorption (TPD)

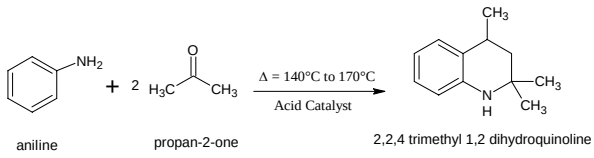
Temperature Programmable Desorption (NH_3-TPD) performed on the catalyst divulges it to be acidic as depicted by the adsorption of ammonia gas as well as the distribution of surface and strength of acid sites. See Fig. 6(a), show NH_3-TPD profile of POSS-SH, which is not functionalized material and two desorption peaks were observed. The peak at temperature lower than 100°C was attributed to the physically adsorbed NH_3 [67]-[68], and other one desorption peaks in the range of 170°C –200°C were related to non acid-functionalized material. See Fig. 6(b), show NH_3-TPD profile of POSS-SO_3H, which is functionalized material and two desorption peaks were observed. The desorption peaks at 140°C –200°C represent increase in the *acid strength.*



Figs. 6. TPD analysis of POSS before (a) and after functionalization (b)

III.1.6. Application of Catalyst for Skraup Cyclization Reaction

Our catalyst is acidic nature so we choose the reaction as depicted below (see Scheme 1) was carried out at different reaction conditions in a laboratory autoclave. The reaction parameters were optimized to determine the optimum speed of agitation, molar ratio of reactants, catalyst loading and temperature



Scheme 1. *Skraup Cyclization reaction*

Parameters, Temperatures were varied from 140°C to 170°C, rotation speeds from 800 rpm to 1400 rpm, molar

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ratio was varied from 1:3 to 1:9 and catalyst loading was varied from 0.01 g/cm3 to 0.03 g/cm^3.

III.2. Proposed Reaction Mechanism

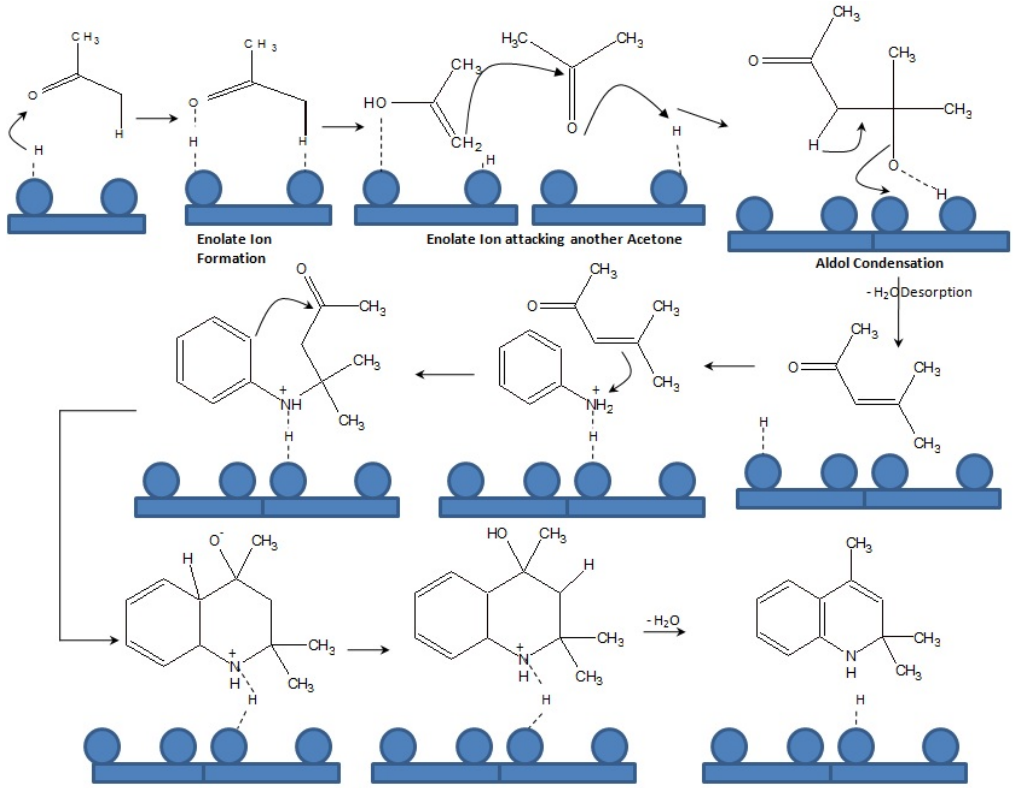
Both the alcohol and acid get adsorbed on the catalyst sites and the reaction proceeds though cyclization reaction of aniline and acetone as shown in plausible mechanism (see Scheme 2).

III.3. Kinetic Study

III.3.1. Effect of Speed of Agitation

The speed of agitation determines the relative effect of external mass transfer resistance. Greater the agitation speed, lesser will be the resistance due to external mass transfer and hence it will not be the rate-determining step in the reaction. The effect of the speed of agitation (see Fig. 7) was studied by varying from 800 to 1400 rpm, under analogous reaction conditions. The conversion of aniline, the limiting reactant, at different intervals of time is shown in Fig. 7.

It was observed that the conversion of aniline was practically the same beyond 1000 rpm, which ensure that external mass-transfer effects did not persuade the reaction rate. To be on secure region, all further experiments were conducted at 1000 rpm.



Scheme 2. Plausible cyclization reaction mechanism

III.3.2. Development of Mechanistic Model and Kinetics of the Reaction

In the absence of both external mass transfer and intraparticle diffusion resistances, it is possible to develop a kinetic model. It is assumed that 2naphthol (A) and dimethyl carbonate (B) adsorb on catalytic site, so we propose the Langmuir-Hinshelwood-Hougen-Watson (LHHW) Model for the reaction mechanism. Scheme 2 depicts the catalytic cycle. This model has been found to work well for initial rate data for reactions carried out on solid acid catalysts where surface adsorption and desorption are weak [69]-[75].

The steps involved in the mechanism are:

1. Adsorption of Aniline (A) on a vacant acidic site (S)

$$A + S \overset{K_A}{\leftrightarrow} A.S \tag{1}$$

This step is assumed to be fast; hence it is taken to be at equilibrium. Therefore, we have:

$$C_{A.S} = K_A C_A C_S \tag{2}$$

2. Adsorption of Acetone (B) on a vacant acidic site (S)

$$B + S \overset{K_B}{\leftrightarrow} B.S \tag{3}$$

This step is assumed to be fast; hence it is taken to be at equilibrium. Therefore, we have:

$$C_{B.S} = K_B C_B C_S \tag{4}$$

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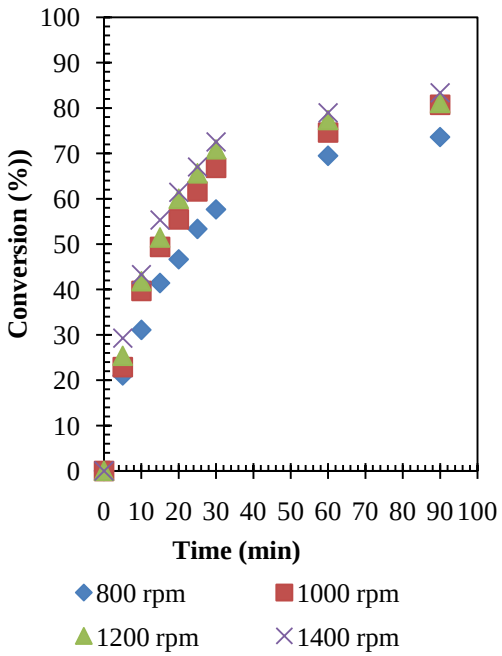

Fig. 7. Aniline: Acetone (1:5), n-decane 2 µl, Temperature 160°C, Catalyst loading 0.03 g/cm^3

3. Surface reaction of A.S with B.S in the vicinity of the site leading to formation of the intermediate I which reacts with another adsorbed species AS

$$A.S + B.S \overset{k_1}{\rightarrow} I.S + W.S \tag{5}$$

$$I.S + A.S \overset{k_2}{\rightarrow} C.S + W.S \tag{6}$$

The steps involving the surface reactions are assumed to be the rate determining step for the overall reaction and initially we assume these reactions to be irreversible.

Also, by steady state approximation, we assume the rate of change of concentration of intermediate *I* as zero.

Therefore, we have:

$$r_{I.S} = k_1 C_{A.S} C_{B.S} - k_2 C_{I.S} C_{A.S} = 0 \tag{7}$$

$$C_{I.S} = \frac{k_1 C_{B.S}}{k_2} \tag{8}$$

If step 6 is assumed to be rate determining, the all other steps are in quasi-equilibrium.

4. Desorption of products from catalyst site

$$C.S \overset{1/K_C}{\longleftrightarrow} C + S \tag{9}$$

$$2W.S \overset{1/K_W}{\longleftrightarrow} 2W + 2S \tag{10}$$

Again, these steps are assumed to be fast, and thus we have:

$$C_{C.S} = K_c C_C C_s \tag{11}$$

$$(C_{W.S})^2 = K_W (C_W)^2 (C_S)^2 \tag{12}$$

or:

$$C_{W.S} = K'_W C_W C_s \tag{13}$$

Now, we have:

$$r_{AS} = -\frac{dC_{AS}}{dt} = k_2 C_{A.S} C_{I.S} \tag{14}$$

From the equations of adsorption of both the reactants we have:

$$r_A = -K_A C_S \frac{dC_A}{dt} = \\ = k_2 (K_A C_A C_S)\left(\frac{k_1 K_B C_B C_S}{k_2}\right) \tag{15}$$

$$r_A = (k_1 K_B C_A C_B) C_s \tag{16}$$

The number of available active sites changes during the progression of the reaction. So, we can relate amount of catalyst in terms of total catalytic sites only. Thus, we have:

$$C_t = C_{A.S} + C_{B.S} + C_{C.S} + C_{W.S} + C_{IS} + C_S \tag{17}$$

$$C_t = K_A C_A C_S + K_B C_B C_S + K_c C_C C_s + \\ + K'_W C_W C_s + \frac{k_1 C_{B.S}}{k_2} + C_s \tag{18}$$

$$C_t = K_A C_A C_S + K_B C_B C_S + K_c C_C C_s + \\ + K'_W C_W C_s + \frac{k_1 K_B C_B C_S}{k_2} + C_s \tag{19}$$

Hence:

$$C_S = \frac{C_t}{\left[\begin{matrix}1 + K_A C_A + K_B C_B + K_C C_C + \\ + K'_W C_W + \frac{k_1 K_B C_B}{k_2}\end{matrix}\right]} \tag{20}$$

Substituting the expression for C_s into that for the rate equation:

$$r_A = -\frac{dC_A}{dt} \tag{21}$$

$$r_A = \frac{(k_1 K_B C_A C_B) C_t}{\left[\begin{matrix}1 + K_A C_A + K_B C_B + K_C C_C + \\ + K'_W C_W + \frac{k_1 K_B C_B}{k_2}\end{matrix}\right]} \tag{22}$$

When adsorption and desorption constants are small, the LHHW model converts itself into a power law model:

$$1 + K_A C_A + K_B C_B + K_C C_C + \\ + K'_W C_W + \frac{k_1 K_B C_B}{k_2} \approx 1 \tag{23}$$

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This implies:

$$r_A = (k_1 K_B C_A C_B) C_t \quad (24)$$

Since the total number of sites is proportional to the catalyst loading, w:

$$C_t \propto w \quad (25)$$

We can define an effective rate constant k':

$$r_{A,initial} = -\frac{dC_A}{dt} = k' w C_A C_B \quad (26)$$

Now, due to very high mole ratio 1:7 (Aniline: Acetone), we can safely assume that concentration of acetone (C_B) remains constant. When all adsorption equilibrium constants are very small, and for $C_{B0} >> C_{A0}$, hence, effective rate constant k can be defined as:

$$r_{A,initial} = -\frac{dC_A}{dt} = kC_A \quad (27)$$

Therefore it is a *pseudo first order* reaction.

Let X_A be the fractional conversion of the limiting reagent A. Then:

$$C_A = C_{A0}(1 - X_A) \quad (28)$$

$$-\frac{dC_A}{dt} = kC_{A0}(1 - X_A) \quad (29)$$

$$C_{A0}\frac{dX_A}{dt} = kC_{A0}(1 - X_A) \quad (30)$$

By integrating the above equation:

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)} = k \int_0^t dt \quad (31)$$

We get:

$$-\ln(1 - X_A) = kt \quad (32)$$

Hence, if it follows the LHHW model (see Fig. 11), the graph of $-\ln(1-X_A)$ versus t should give a straight line. Fig. 11 represents the aforementioned quantities for different temperatures.

III.3.3. Effect of Catalyst Loading

In the absence of external mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire liquid phase volume, which is due to the proportional increase in the number of active sites. Further reactions were carried out with 0.024 g/cm3 catalyst loading. The catalyst loading was varied over a range of 0.01 – 0.03 g/cm3 under similar reaction conditions (see Fig. 8).

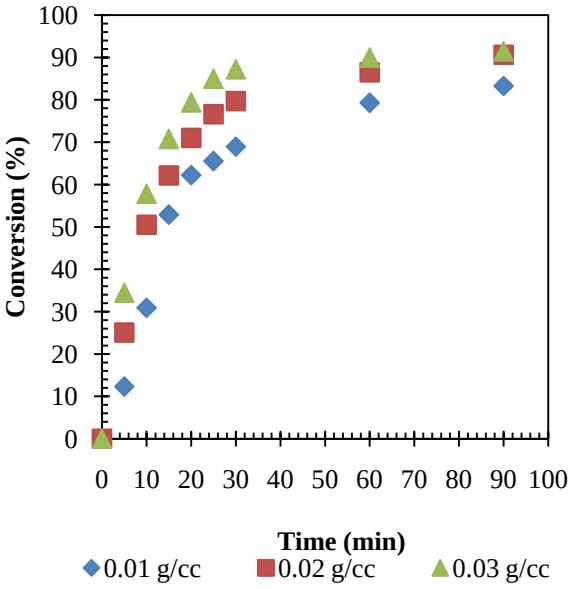

Fig. 8. Speed of agitation = 1000 rpm, Aniline: Acetone (1:5), n-decane 2 µl, Temperature 160°C

This conversion increases with increasing catalyst loading, which can be attributed to the proportional increase in the number of active sites available. However, beyond loading of 0.02 g/cm^3, there was not any significant increase in the conversion observed.

III.3.4. Effect of Mole Ratio(Aniline:Acetone)

Under solvent-less conditions, the effect of mole ratio of aniline to acetone was studied from 1:3 to 1:9. The catalyst loading was kept at 0.02g/cm^3 and speed of agitation at 1000 rpm. The most suitable mole ratio was found to be 1:7 with aniline as the limiting reagent as shown in Figure 9.

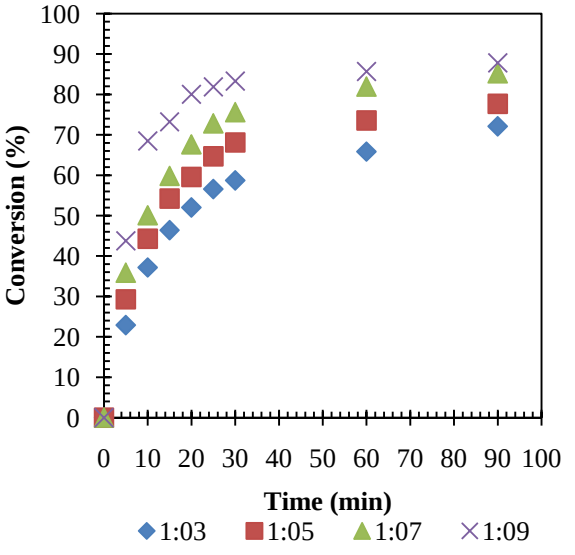

Fig. 9. Speed of agitation = 1000 rpm, n-decane 2 µl, Catalyst loading 0.02 g/cm^3, Temperature 160°C

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As the concentration of acetone increases, the number of available sites for adsorption of aniline decreases, and there is not any considerable increase in conversion and yield above a mole ratio of 1:7

III.3.5. Effect of Temperature

The effect of temperature (see Fig. 10) was studied at four different temperatures in the range 140–170°C under similar reaction conditions as shown in Fig 10. For a specific conversion of aniline, the reaction rate increases with temperature rise.

Therefore, it was found that the conversion increased significantly with increase in temperature. There was marginal increase in conversion at 170°C to that of 160°C; this would suggest a kinetically controlled mechanism. Hence the optimum temperature was determined to be 160°C.

III.3.6. Arrhenius Plot

In order to determine the energy of activation, ln(k) is plotted against the inverse of temperature in accordance with Arrhenius' Law:

$$k = Ae^{-\frac{E_a}{RT}} \quad (33)$$

$$ln(k) = ln(A) - \frac{E_a}{RT} \quad (34)$$

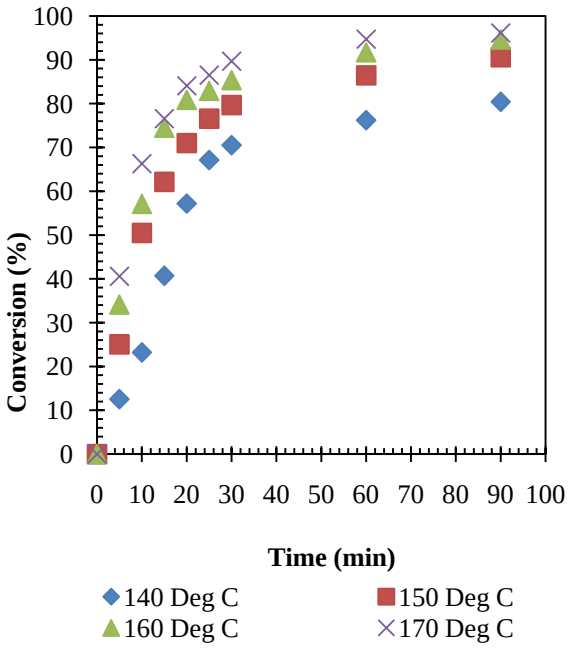

Fig. 10. Speed of agitation = 1000 rpm, n-decane 2 µl, Catalyst loading 0.02 g/cm^3, Aniline: Acetone (1:7)

An Arrhenius plot was used to estimate the apparent activation energy of the reaction (Fig. 12). The apparent activation energy was computed to be 11.054 kcal/mol, which indicates intrinsically kinetically controlled reaction.

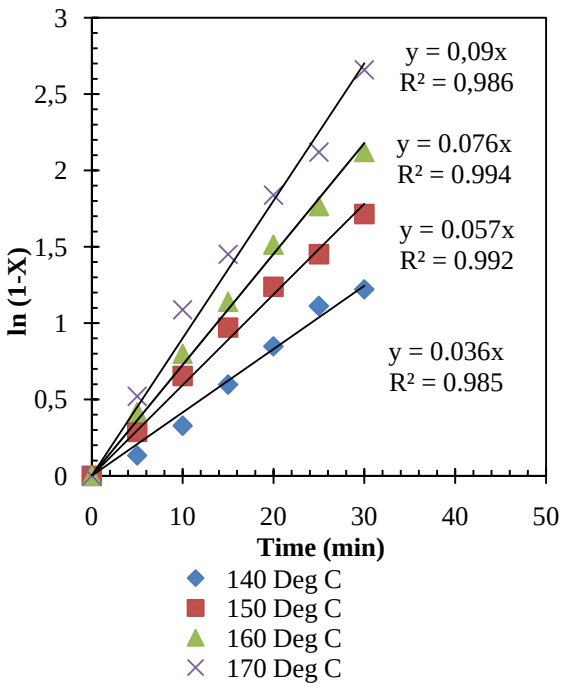

Fig. 11. Validation of LHHW model

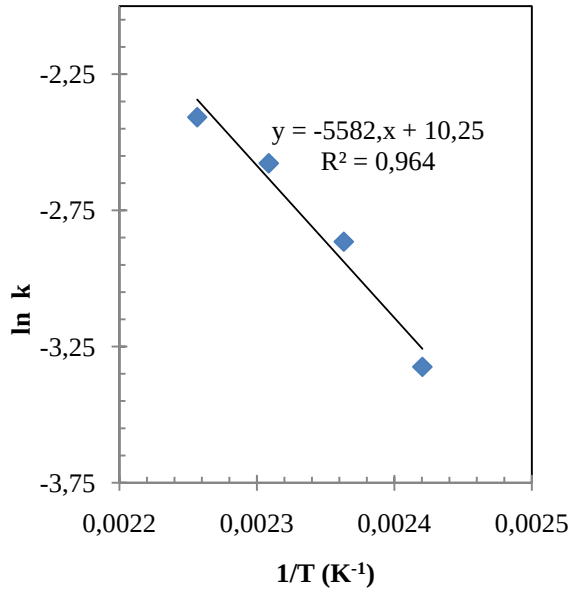

Fig. 12. Arrhenius plot

III.3.7. Stability of Catalyst

The reusability of the catalyst was studied, after completion of reaction the catalyst was recovered and washed with methanol for two to three times by refluxing the used catalyst in ethanol for 30 min in order to remove any adsorbed materials, like product, remaining reactants from within the pores. It was separated and dried at 373 K overnight. This process was repeated for every reuse of catalyst. The little loss in conversion after second reuse was found due to the adsorption of molecule on the

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catalyst surface. Recyclability of catalyst was studied for three cycles. About 80–85% catalysts were recovered at the end of the reaction. Out of the total recovered catalyst from previous batch, 70% catalyst used for next reaction with 30% fresh catalyst so as to make desired quantity of standard batch. The catalyst could be reused with some decrease in conversion (see Table II) for three cycles after fresh use. Thus, POSS-SO_3H was proved to be superior catalyst for cyclization reaction.

TABLE II
CATALYST REUSABILITY STUDIES

\	*Conversion*
Fresh	94
1st reuse	86
2nd reuse	81
3rd reuse	76

IV. Conclusion

2,2,4- Trimethyl-1,2-dihydroquinoline has been successfully synthesized by the Skraup Cyclization reaction of aniline and acetone carried out with a new acid catalyst, POSS-SO_3H, in solvent free conditions with very high conversions at a relatively shorter time period, with various characterization of catalyst like TPD, TGA, SEM, XRD and FT-IR spectroscopy. The effects of various parameters on the rates of the reactions were discussed. A pseudo first order rate equation for the reaction mechanism was successfully developed. The apparent activation energy 11.054 kcal/mol was estimated, as value of the activation energy authorize that the reaction is intrinsically kinetically controlled.

Acknowledgements

GDY acknowledges support for personal chairs from the Darbari Seth Professor Endowment and R. T. Mody Distinguished Professor Endowment, and J. C. Bose National Fellowship from Department of Science and Technology, Government of India. RPK acknowledges the Department of Atomic Energy (DAE), Government of India for awarding the Research Fellowship. SH acknowledge the Indian Academy of Sciences (IASc) for awarding the summer trainee fellowship.

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