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Preparation, Characterization and First Application of Aerosil Silica Supported Acidic Ionic Liquid as a Reusable Heterogeneous Catalyst for the Synthesis of 2,3-Dihydroquinazolin-4(1*H*)-ones

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A new heterogeneous acidic catalyst was successfully prepared by impregnation of silica (Aerosil 300) by an acidic ionic liquid, named 1-(4-sulfonic acid)butylpyridinium hydrogen sulfate [PYC_4SO_3H][HSO_4], and characterized using FT-IR spectroscopy, the N_2 adsorption/desorption analysis (BET), thermal analysis (TG/DTG), and X-ray diffraction (XRD) techniques. The amount of loaded acidic ionic liquid on Aerosil 300 support was determined by acid-base titration. This new solid acidic supported heterogeneous catalyst exhibits excellent activity in the synthesis of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones by cyclocondensation reaction of 2-aminobenzamide with aromatic aldehydes under solvent-free conditions and the desired products were obtained in very short reaction times with high yields. This catalyst has the advantages of an easy catalyst separation from the reaction medium and lower problems of corrosion. Recycling of the catalyst and avoidance of using harmful organic solvent are other advantages of this simple procedure.

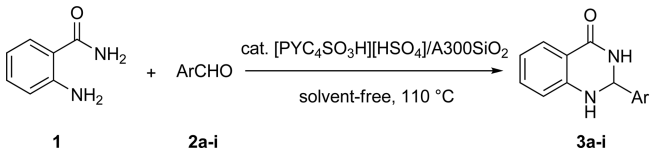
Key Words : Supported acidic ionic liquid, Aerosil silica, Heterogeneous catalysis, Solvent-free conditions

Introduction

During the recent years, the use of reusable heterogeneous catalysts has received considerable importance in organic synthesis because of their environmental, economical and industrial aspects.[1-4] Preparing heterogeneous catalysts by supporting the homogenous precursors on solid support is one of the important routes for developing novel heterogeneous catalysts. In most of these cases, the supported catalysts so prepared could provide advantages over their unsupported counterparts in terms of separation, reusability, and particularly, the ability to provide practical conveniences in a continuous system that is valued in industry.[5-7] In supported catalysts, the catalytic behavior of the catalyst is strongly dependent on support properties. Among the various supported catalysts, particularly, alumina and silica supported reagents have advantages of low cost, ease of preparation, and catalyst recycling.[8-11]

Ionic liquids (ILs), which are organic salts having melting points below 100 °C, have attracted in the last decade much attention in organic chemistry as catalysts or solvents.[12-15] Their remarkable chemical and physical characteristics encouraged both academic and industrial chemists to explore their use in diverse domains such as chemical analysis,[16] liquid-liquid extraction processes,[17] electrochemistry,[18] engineering fluids,[19] and as recyclable alternatives to aprotic solvents in organometallic reactions.[20] SO_3H-functionalized ILs can be used as highly efficient acid catalysts and have been receiving extensive interest as green substitute for H_2SO_4, HF and $AlCl_3$ catalysts in chemical processes.[21-23] However, compared to pure acidic IL catalysts, the supported acidic ILs show additional advantages, which include the facilitation of catalyst separation from reaction system, decreased consumption of IL and lower contamination of product.

2,3-Dihydroquinazolin-4(1*H*)-ones are an important class of fused heterocycles with a wide range of pharmacological and biological activities including antifertility, antibacterial, antitumor, and antifungal activity.[24-26] A small number of quinazolinones have been reported as potent chemotherapeutic agents in the treatment of tuberculosis.[27] In addition, quinazolinone moiety is a building block for approximately 150 naturally occurring alkaloids, such as glycosminine,[28] deoxyvasicinone,[29] and piriqualone.[30] Therefore, considerable efforts have been made to explore new simple and direct approaches towards the construction of 2,3-dihydroquinazolin-4(1*H*)-ones skeletons. The typical procedure for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones involves the condensation reaction of anthranilamides with aldehydes or ketones using various promoting agents, such as TBAB,[31] $Sc(OTf)_3$,[32] $Ga(OTf)_3$,[33] Montmorillonite K-10,[34] and I_2.[35] Other methods such as condensation of *o*-aminobenzamide with benzyl followed by base catalyzed hydrolysis,[36] reductive cyclization of *o*-nitrobenzamide or *o*-azidobenzamide with aldehydes and ketones using metallic samarium in the presence of iodine,[37] reductive desulfurization of 2-thioxo-3*H*-quinazolin-4-ones with nickel boride in dry methanol,[38] and one-pot conversion of 2-nitro-*N*-arylbenzamides to 2,3-dihydroquinazolin-4(1*H*)-ones using $SnCl_2$,[39] are also reported for the synthesis of these compounds. Though these methodologies are quite useful, most of the methods encounter some limitations, such as expensive catalysts, long reaction times, toxic organic solvents and harsh reaction conditions. Therefore, the development of simple, efficient, clean, high-



Scheme 1. Synthesis of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones catalyzed by $[PYC_4SO_3H][HSO_4]/A300SiO_2$.

yielding, and environmentally friendly approaches using new catalysts for the synthesis of these compounds is an important task for organic chemists.

Prompted by these findings and due to our interest in the applications of reusable catalysts in organic reactions[40-47] herein firstly we report the preparation of a new supported acidic IL by impregnation of silica (Aerosil 300) by 1-(4-sulfonic acid)butylpyridinium hydrogen sulfate (denoted as $[PYC_4SO_3H][HSO_4]/A300SiO_2$), and then investigate its catalytic activity in the synthesis of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones **3a-i** by cyclocondensation of 2-aminobenzamide **1** with aromatic aldehydes **2a-i** under solvent-free conditions (Scheme 1).

Experimental

All chemicals were available commercially and used without additional purification. Aerosil 300 (300 m^2/g) was obtained from Evonic Degussa GmbH company. The IL, $[PYC_4SO_3H][HSO_4]$, was synthesized according to the literature.[48] Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. Thermal gravimetric and differential thermal gravimetry (TGA/DTG) analyses were performed using air as oxidant at the heating rate of 5 °C min^{-1} in TGA-50, Shimadzu system. The BET surface area of the material was measured by nitrogen adsorption isotherm method with Quantachrome instrument model Autosorb1, USA. X-ray diffraction (XRD) was performed with a D8-Advance, Bruker X-ray diffractometer using graphite monochromatized high-intensity CuKα radiation (k = 1.5406 Å). The ^1H NMR (400 & 500 MHz) spectra were recorded with Bruker 400 & 500 spectrometers.

Preparation of $[PYC_4SO_3H][HSO_4]/A300SiO_2$. The catalyst was prepared by impregnation method. Silica (Aerosil 300, 1.0 g) was added to a solution of $[PYC_4SO_3H][HSO_4]$ (0.75 g) in methanol (20 mL). The mixture was stirred at room temperature for 20 h to adsorb IL on surface of support. The methanol was removed with rotary evaporator and the resulting solid powder was washed with cold chloroform, and dried in vacuo at 100 °C for 2 h. The amount of H^+ in the $[PYC_4SO_3H][HSO_4]/A300SiO_2$ determined by acid-base titration was 1.5 mmol/g.

General Procedure for the Synthesis of 2-Aryl-2,3-dihydroquinazolin-4(1*H*)-ones 3a-i Catalyzed by $[PYC_4SO_3H][HSO_4]/A300SiO_2$. A mixture of 2-aminobenzamide **1** (1 mmol), aromatic aldehyde **2a-i** (1 mmol) and $[PYC_4SO_3H][HSO_4]/A300SiO_2$ (0.03 g) was heated in the oil bath at 110 °C for 10-14 min. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and hot chloroform was added. The catalyst was insoluble in hot chloroform and could therefore be recycled by a simple filtration. The filtrate was heated in vacuo to evaporate the solvent. The solid residue was collected and recrystallized from chloroform to give compounds **3a-i** in high yields.

Recycling and Reusing of the Catalyst. Due to the fact that the catalyst was insoluble in hot chloroform, it could therefore be recycled by a simple filtration. The separated catalyst was washed with cold chloroform, dried in vacuo at 100 °C for 2 h, and reused in another reaction. The catalyst could be used at least three times with only slight reduction in its catalytic activity.

Results and Discussion

Characterization of the Catalyst. The catalyst $[PYC_4SO_3H][HSO_4]/A300SiO_2$ prepared by impregnation of silica (Aerosil 300) support by $[PYC_4SO_3H][HSO_4]$ was characterized by FT-IR spectroscopy, the N_2 adsorption/desorption analysis (BET), X-ray diffraction (XRD) and thermal analysis (TG/DTG) techniques.

The FT-IR absorption bands assigned to $[PYC_4SO_3H][HSO_4]$, silica (Aerosil 300), and $[PYC_4SO_3H][HSO_4]/A300SiO_2$ are shown in Figure 1. The locations of featured peaks for the sample of supported catalyst (Fig. 1(c)) prepared in this work were in well agreement with those for $[PYC_4SO_3H][HSO_4]$ (Fig. 1(a)), and silica (Aerosil 300)

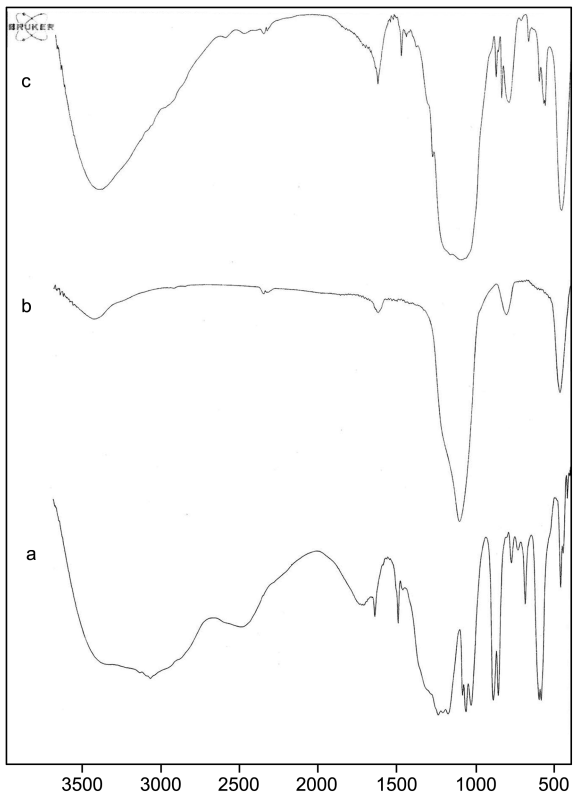


Figure 1. FT-IR spectra of (a) $[PYC_4SO_3H][HSO_4]$, (b) Silica (Aerosil 300), (c) $[PYC_4SO_3H][HSO_4]/A300SiO_2$.

Table 1. N_2 adsorption results of silica (Aerosil 300), and $[PYC_4SO_3H][HSO_4]/A300SiO_2$ in BET measurements

Sample	Specific surface area ($m^2.g^{-1}$)			Pore diameter (Å)		Pore volume ($mL.g^{-1}$)	
	BET	BJH_{Ads}	DH_{Ads}	BJH_{Ads}	DH_{Ads}	BJH_{Ads}	DH_{Ads}
silica (Aerosil 300)	83.80	80.91	82.54	13.97	13.97	0.141	0.139
$[PYC_4SO_3H][HSO_4]/A300SiO_2$	70.50	74.27	75.76	13.92	13.92	0.222	0.217

(Fig. 1(b)) which indicates the IL has been adsorbed well on the Aerosil 300 surface.

The data of specific surface area, pore size and pore volume of $[PYC_4SO_3H][HSO_4]/A300SiO_2$ and silica (Aerosil 300) are presented in Table 1. The surface area of supported catalyst decreased compared to its parent support, but still showed very high value. The reduction in the surface area of supported catalyst may be due to the blockage of smaller pores by active species and shows the impregnation of silica (Aerosil 300) by $[PYC_4SO_3H][HSO_4]$. The N_2 adsorption-desorption isotherm of the supported catalyst is shown in Figure 2. The majority of isotherms have been grouped into six types by IUPAC classification (I, II, III, IV, V, and VI),[49] but only types I, II, and IV are commonly found in the adsorption on polar materials. The shape of the isotherm of the supported catalyst in this paper is type II. Type II isotherm is the normal form of isotherm that monolayer coverage is followed by multilayering at high relative pressures, and is normally obtained with non-porous or macroporous adsorbents. The adsorption/desorption isotherms in Figure 2 are overlapped and the hysteresis loop has been disappeared.

Thermal gravimetric (TGA) and differential thermal gravimetry (DTG) analysis of the $[PYC_4SO_3H][HSO_4]/A300SiO_2$ was investigated by raising its temperature at the rate of 5 °C/min in air up to 1000 °C to analyze its thermal decomposition behavior. Figure 3 shows the TGA/DTG curves of the prepared $[PYC_4SO_3H][HSO_4]/A300SiO_2$. Two main stages of weight loss are observed. The first small weight loss centered at 52.20 °C is assigned to the loss of physically adsorbed water molecules and the second weight loss centered at 333.93 °C is probably due to decomposition or removal of $[PYC_4SO_3H][HSO_4]$.

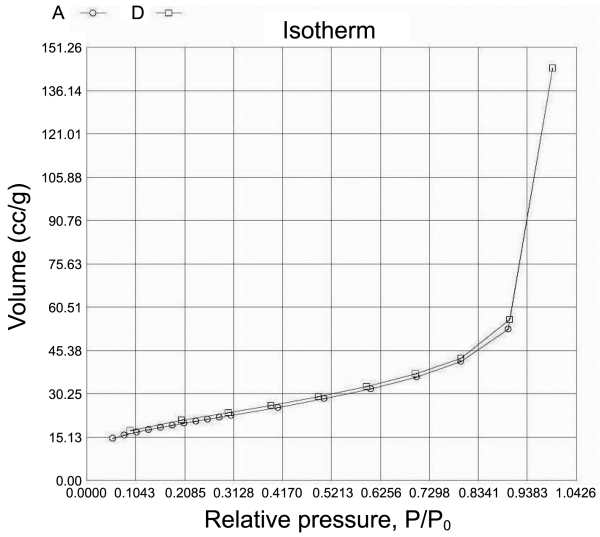


Figure 2. N_2 adsorption-desorption isotherm of $[PYC_4SO_3H][HSO_4]/A300SiO_2$.

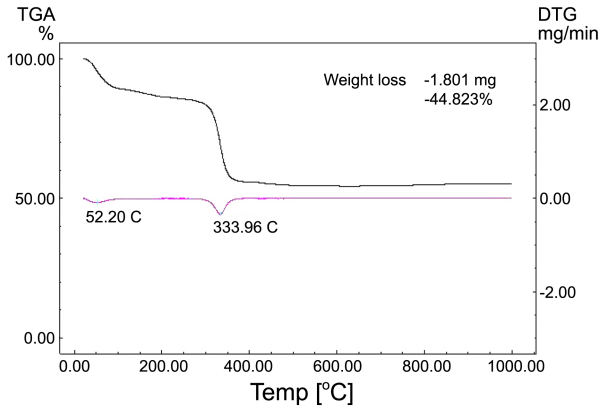


Figure 3. TGA and DTG curves of $[PYC_4SO_3H][HSO_4]/A300SiO_2$.

The XRD pattern of the silica (Aerosil 300), and $[PYC_4SO_3H][HSO_4]/A300SiO_2$ are also presented in Figure 4. These XRD patterns indicate that $[PYC_4SO_3H][HSO_4]$ over the surface of silica (Aerosil 300) is either amorphous or too small to be detected by XRD method and or that is highly dispersed on the support surface.

Catalytic Evaluation of $[PYC_4SO_3H][HSO_4]/A300SiO_2$ in the Synthesis of 2-Aryl-2,3-dihydroquinazolin-4(1*H*)-ones. The catalytic activity of $[PYC_4SO_3H][HSO_4]/A300SiO_2$

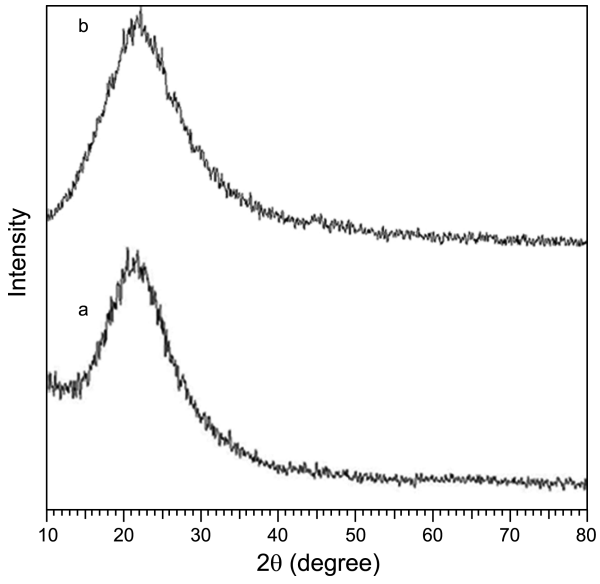


Figure 4. XRD patterns of (a) Silica (Aerosil 300) and (b) $[PYC_4SO_3H][HSO_4]/A300SiO_2$.

Table 2. Effect of $[PYC_4SO_3H][HSO_4]/A300SiO_2$ amount, solvent, temparature, and different catalysts on the model reaction[a]

Entry	Catalyst	Catalyst amount (g)	Solvent	T (°C)	Time (min)	Yield (%)[b]
1	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	None	Solvent-free	110	120	Trace
2	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.02	Solvent-free	50	30	48
3	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.02	Solvent-free	70	30	56
4	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.02	Solvent-free	90	10	60
5	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.02	Solvent-free	110	10	72
6	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	Solvent-free	50	30	62
7	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	Solvent-free	70	30	69
8	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	Solvent-free	90	10	71
9	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	Solvent-free	110	10	90
10	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	Solvent-free	130	10	90
11	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.05	Solvent-free	110	10	80
12	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.07	Solvent-free	110	10	77
13	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	H_2O	Reflux	45	67
14	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	EtOH	Reflux	45	83
15	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	CH_3CN	Reflux	45	48
16	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	CH_2Cl_2	Reflux	45	79
17	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	$CHCl_3$	Reflux	45	75
18	$[PYC_4SO_3H][HSO_4]/A300SiO_2$	0.03	CH_3CO_2Et	Reflux	45	70
19	$NH_4H_2PO_4/Al_2O_3$	0.03	Solvent-free	110	30	90
20	$[TBA]_2[W_6O_{19}]$	0.03	Solvent-free	110	80	71
21	PPA/Al_2O_3	0.03	Solvent-free	110	35	83
22	CBSA	0.03	Solvent-free	110	85	89
23	$[MIMC_4SO_3H][HSO_4]$	0.03	Solvent-free	110	90	69
24	$PPA\text{-}SiO_2$	0.03	Solvent-free	110	25	85
25	$[PYC_4SO_3H][HSO_4]$	0.03	Solvent-free	110	30	77

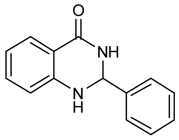
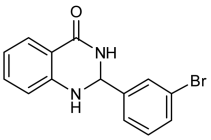
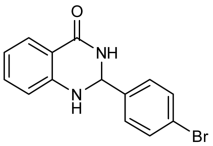
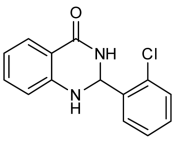
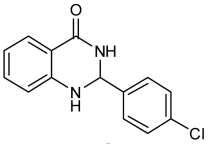
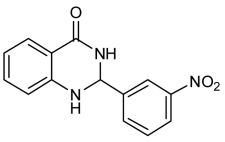
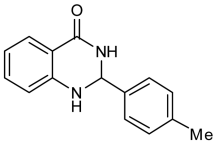
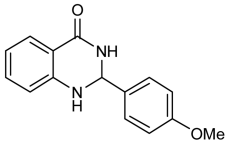
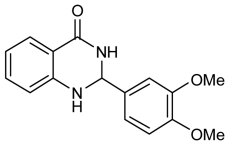
[a]2-aminobenzamide (1 mmol), and 4-chlorobenzaldehyde (1 mmol). [b]The yields were calculated based on 4-chlorobenzaldehyde and refer to the pure isolated product.

as a solid acidic supported catalyst was evaluated in the synthesis of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones. We first studied the reaction between 2-aminobenzamide (1 mmol) and 4-chlorobenzaldehyde (1 mmol) by screening the reaction conditions. In order to determine the optimum conditions, we examined the influence of the amount of $[PYC_4SO_3H][HSO_4]/A300SiO_2$, solvent, and the reaction temperature (Table 2). It could be seen that the shortest time and best yield were obtained in solvent-free conditions (entry 9). It was also found that the yield of compound **3e** was strongly affected by the catalyst amount and reaction temperature in solvent-free conditions. Without any catalyst, the yield was poor even for a long time at 110 °C. Increasing the amount of the catalyst up to 0.03 g, increased the yield of the product **3e**, whereas further increase in catalyst amount was found to have an inhibitory effect on formation of the product (entries 11 & 12). For the temperatures evaluated (50, 70, 90, 110 and 130 °C), the product **3e** was obtained in moderate yields at 50, 70 and 90 °C, and in high yield at 110 °C. Increasing the reaction temperature to 130 °C did not improve the yield (entry 10).

To show the merit of the present methodology, the effect of other catalysts such as alumina supported ammonium dihydrogenphosphate ($NH_4H_2PO_4/Al_2O_3$), tetrabutylammonium hexatungstate ($[TBA]_2[W_6O_{19}]$), alumina supported polyphosphoric acid (PPA/Al_2O_3), carbon-based solid acid (CBSA), 3-methyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate $[MIMC_4SO_3H][HSO_4]$, silica gel-supported polyphosphoric acid ($PPA\text{-}SiO_2$), and 1-(4-sulfonic acid)butylpyridinium hydrogen sulfate ($[PYC_4SO_3H][HSO_4]$), that are of interest in our group,[3,4,6,13,42-44] was also investigated in the above model reaction in optimized conditions. The results are shown in Table 2 (entries 19-25). As depicted, $[PYC_4SO_3H][HSO_4]/A300SiO_2$ proved to be the better catalyst than others in terms of reaction time and yield. Although there is no significant difference between $[PYC_4SO_3H][HSO_4]/A300SiO_2$, $NH_4H_2PO_4/Al_2O_3$, and CBSA as catalyst in terms of reaction yield, but the reaction time is shorter in the presence of $[PYC_4SO_3H][HSO_4]/A300SiO_2$. Also, $[PYC_4SO_3H][HSO_4]/A300SiO_2$ as a supported IL gave the better result than pure IL, $[PYC_4SO_3H][HSO_4]$, probably due to increase the active site accessibility in supported form. Consequently, all subsequent reactions were carried out in the presence of 0.03 g of $[PYC_4SO_3H][HSO_4]/A300SiO_2$ as catalyst at 110 °C under solvent-free conditions.

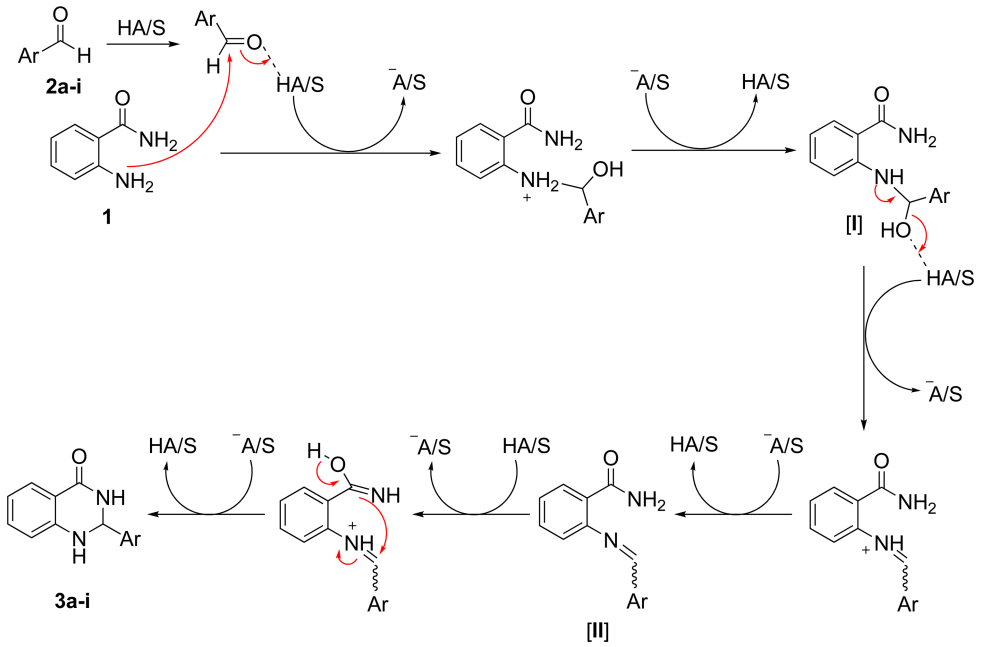
In order to evaluate the general character of this model reaction, we included a range of other aromatic aldehydes in the reaction of 2-aminobenzamide under the optimized reaction conditions. In all cases, the expected products were obtained in high yields in short reaction times. The results are given in Table 3. As shown, aromatic aldehydes with substituents carrying either electron-donating or electron-

Table 3. Synthesis of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones **3a-i** using $[PYC_4SO_3H][HSO_4]$/A300SiO_2 as catalyst[a]

Entry	Ar	Products[b]	Time (min)	Yield (%)[c]	mp ºC		Ref.
					Found	Reported	
1	C_6H_5	 **3a**	10	83	222-223	221-223	31
2	3-BrC_6H_4	 **3b**	10	84	223-225	229-230	35
3	4-BrC_6H_4	 **3c**	10	88	195-198	197-199	31
4	2-ClC_6H_4	 **3d**	10	88	225-226	230-231	35
5	4-ClC_6H_4	 **3e**	10	90	203-205	205-206	33
6	3-$O_2NC_6H_4$	 **3f**	12	80	192-194	180-182	35
7	4-MeC_6H_4	 **3g**	10	81	229-230	231-232	31
8	4-$MeOC_6H_4$	 **3h**	10	86	184-185	178-180	34
9	3,4-$(MeO)_2C_6H_3$	 **3i**	14	81	205-207	210-213	34

[a]2-aminobenzamide (1 mmol), aromatic aldehyde (1 mmol), and $[PYC_4SO_3H][HSO_4]$/A300SiO_2 (0.03 g) at 110 ºC under solvent-free conditions. [b]All the products were characterized by IR spectral data and comparision of their melting points with those of authentic samples. Also, the structures of some products were confirmed by ^{1}H NMR spectral data. [c]The yields were calculated based on aromatic aldehyde and refer to the pure isolated product.

withdrawing groups reacted successfully to give the products in high yields. Like most reports in the synthesis of 2,3-dihydroquinazoline-4(1*H*)-ones,[31-35] the position and electronic nature of the substituent on the phenyl ring of aryl-



Scheme 2. Plausible mechanism for the formation of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones in the presence of $[PYC_4SO_3H][HSO_4]$/$A300SiO_2$ ≡ HA/S as catalyst.

aldehydes had no significant effect on the reaction. For example, although methyl-, methoxy- and bromo- substitutents have different electron effects on benzaldehydes, similar reaction rate and yield were observed.

A plausible mechanism may proceed as depicted in Scheme 2. The addition of nucleophiles to the aldehydes is promoted by protonation of the carbonyl group using a Brønsted acid enhancing the electrophilicity of this moiety. Therefore, it is proposed that, at first, the reaction starts through nucleophilic attack of the amino group in 2-aminobenzamide at the activated carbonyl group in arylaldehyde by $[PYC_4SO_3H][HSO_4]/A300SiO_2$ ≡ HA/S as a supported Brønsted acid. It seems that the reaction proceeds through intermediate [**I**], such that after dehydration, the imine intermediate [**II**] is produced. The part of amide in imine intermediate [**II**] could be converted into its tautomer in the presence of HA/S. On the other hand, the part of imine in this intermediate could be activated by HA/S. Thus, intermediate [**II**] could be converted to 2,3-dihydroquinazolin-4(1*H*)-ones **3a-i** by intramolecule nucleophile attack of the nitrogen on activated imine carbon. However, attempts to isolate the intermediates [**I**] and [**II**] failed after careful monitoring of the reactions.

The stability of the active species has been of concern for solid acids, especially for supported materials. Since 0.03 g $[PYC_4SO_3H][HSO_4]/A300SiO_2$ showed the best results, reusability of this catalyst was investigated in model reaction. Based on our investigations, in polar media, especially water and ethanol, the catalyst has poor reusability, but in solvent-free condition, the reusability of $[PYC_4SO_3H][HSO_4]/A300SiO_2$ was found to be favorable and it could be recovered and subsequently reused several times. It showed a slightly loss of activity after three successive runs (90% for 1st use; 89% for 2nd use; 87% for 3rd use).

Conclusion

In conclusion, a new solid acidic supported catalyst, $[PYC_4SO_3H][HSO_4]/A300SiO_2$, was prepared by impregnation of silica (Aerosil 300) support by $[PYC_4SO_3H][HSO_4]$ and characterized by FT-IR, BET, TG/DTG and XRD techniques. The catalyst showed high catalytic activity in the synthesis of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones by cyclocondensation reaction of 2-aminobenzamide with aromatic aldehydes under solvent-free conditions. Some attractive features of this protocol are high yields, short reaction times, simple procedure, absence of any volatile and hazardous organic solvents, and recyclability and reusability of the catalyst. Further applications of this new catalyst for other reaction systems are currently under investigation.

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