Preparation, Characterization and First Application of Alumina Supported Polyphosphoric Acid (PPA/Al$_2$O$_3$) as a Reusable Catalyst for the Synthesis of 14-Aryl-14*H*-dibenzo[*a, j*]xanthenes

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Alumina supported polyphosphoric acid (PPA/Al$_2$O$_3$) was successfully prepared by impregnation of alumina support by polyphosphoric acid and characterized using FT-IR spectroscopy, the N$_2$ adsorption/desorption analysis (BET), thermal analysis (TG/DTG), and X-ray diffraction (XRD) techniques. The catalytic behavior of this new solid acid supported heterogeneous catalyst was checked in the synthesis of 14-aryl-14*H*-dibenzo[*a, j*]xanthenes by cyclocondensation reaction of β-naphthol and aryl aldehydes under solvent-free conditions. The results showed that the novel catalyst has high activity and the desired products were obtained in very short reaction times with high yields. Moreover, the catalyst can be easily recovered by filtration and reused at least three times with only slight reduction in its catalytic activity.

Key Words : Alumina supported polyphosphoric acid, 14-Aryl-14*H*-dibenzo[*a, j*]xanthenes, Heterogeneous catalysis, Solvent-free conditions

Introduction

The use of homogeneous acid catalysts has some major limitations including no possible reuse, difficulty of products separation, air and moisture sensitivity and low product selectivity.[1] As a result, one of the challenges in the field of catalysis is to replace these homogeneous acid catalysts by non-toxic, non-corrosive, easy to handle and environmentally friendly heterogeneous catalysts. Preparing heterogeneous catalysts by impregnation of a solid support by the homogenous precursors is one of the important routes for developing novel heterogeneous catalysts.[2,3] In most of these cases, the solid supported catalysts 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.[4] In supported catalysts, the catalytic behaviors 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.[5-9]

Xanthenes and dibenzoxanthenes' derivatives are important classes of organic compounds with a large number of naturally occurring, as well as synthetic derivatives, and occupy a prominent position in medicinal chemistry.[10] A number of these compounds have been considered as dyes and fluorescent visualization materials for biomolecules and laser technologies.[11,12] Furthermore, these compounds have been investigated for their agricultural bactericide activity,[13-15] anti-inflammatory effect,[16] and antiviral activity.[17] There are several methods reported in literature for the synthesis of

xanthenes and dibenzoxanthenes such as, palladium catalyzed cyclization of polycyclic aryltriflate esters,[18] and intramolecular trapping of benzynes by phenols.[19] Furthermore, 14-aryl-14*H*-dibenzo[*a, j*]xanthenes and their analogues were prepared by reaction of β-naphthol with 2-naphthol-1-methanol,[20] formamide,[21] carbon monoxide[22] as well as by condensation of β-naphtol with aldehydes using various acid catalysts.[23-27] Many of these methodologies, however, suffer from disadvantages such as unsatisfactory yields, expensive catalysts, long reaction times, toxic organic solvents, and harsh reaction conditions. Therefore, the development of simple, efficient, high-yielding, and environmentally friendly methods using new catalysts for the synthesis of these compounds is still necessary.

As part of our current studies on the development of new routes for the synthesis of organic compounds using reusable catalysts,[28-37] herein we wish to report an efficient, green, and fast method for the synthesis of 14-aryl-14*H*-dibenzo-[*a, j*]xanthenes by condensation of β-naphthol with aryl aldehydes using alumina supported polyphosphoric acid (PPA/Al$_2$O$_3$) as a new solid acid supported catalyst under solvent-free conditions (Scheme 1).
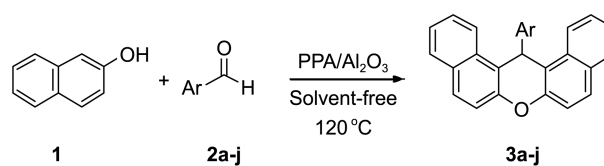
Scheme 1. Synthesis of 14-aryl-14*H*-dibenzo[*a, j*]xanthenes catalyzed by PPA/Al$_2$O$_3$.

Experimental

All chemicals were available commercially and used without additional purification. 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 ^{1}H NMR (500 MHz) spectra were recorded with a Bruker DRX500 spectrometer.

Preparation of PPA/Al$_2$O$_3$. PPA (2.2 g) was charged in the round-bottom flask, and CHCl$_3$ (100 mL) was added. After the mixture was stirred at 50 °C for 1 h, neutral alumina (70-230 mesh, 5.0 g) was added to the solution, and the mixture was stirred for another 4 h. The CHCl$_3$ was removed with rotary evaporator and the resulting solid was washed with cold absolute ethanol, and dried in vacuo at 70 °C for 2 h. The amount of H$^+$ in the PPA/Al$_2$O$_3$ determined by acid-base titration was 0.55 mmol/g.

General Procedure for the Synthesis of 14-Aryl-14*H*-dibenzo[*a,j*]xanthenes 3a-j Using PPA/Al$_2$O$_3$ as Catalyst. A mixture of β-naphthol **1** (2 mmol), aromatic aldehyde **2a-j** (1 mmol), and PPA/Al$_2$O$_3$ (0.030 g, 0.016 mmol of H$^+$) was heated in the oil bath at 120 °C for 5-10 min. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and hot ethyl acetate was added. The catalyst was insoluble in hot ethyl acetate 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 ethanol to give compounds **3a-j** in high yields.

Recycling and Reusing of the Catalyst. Due to the fact that the catalyst was insoluble in hot ethyl acetate, it could therefore be recycled by a simple filtration. The separated catalyst was washed with cold absolute ethanol, dried at 70 °C under vacuum 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

Characterizations of the Catalyst. The catalyst PPA/Al$_2$O$_3$ prepared by impregnation of alumina support by PPA was characterized by FT-IR spectroscopy, the N$_2$ adsorption/desorption analysis (BET), thermal analysis (TG/DTG), and X-ray diffraction (XRD) techniques.

FT-IR spectra of Al$_2$O$_3$, PPA and PPA/Al$_2$O$_3$ are compared in Figure 1. In the IR spectrum of PPA/Al$_2$O$_3$ (Fig. 1(c)), most of the bands of both Al$_2$O$_3$ (Fig. 1(a)), and PPA (Fig.
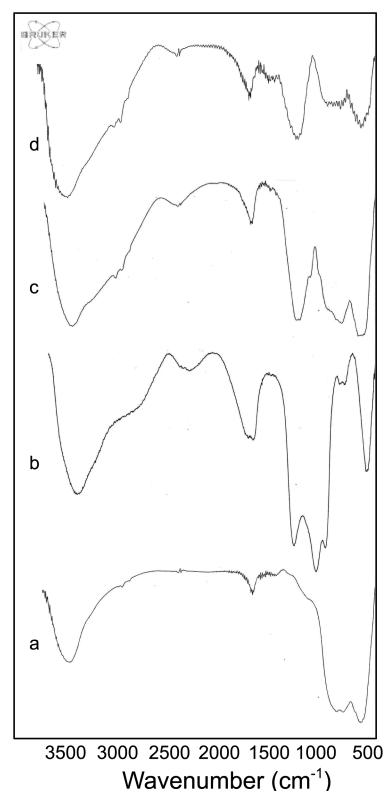

Figure 1. FT-IR spectra of (a) Al$_2$O$_3$, (b) PPA, (c) fresh PPA/Al$_2$O$_3$, (d) recovered PPA/Al$_2$O$_3$.

1(b)), with a slight shift for some of them, are observable which indicates PPA has been adsorbed well on the alumina surface.

The specific surface area of PPA/Al$_2$O$_3$ measured by the BET method and other methods is in the range of 117.0-131.6 m^2/g (Table 1). As shown in Table 1, the sample shows a high specific surface area, medium specific total volume and a small pore diameter. The N$_2$ adsorption-desorption isotherm of the sample is shown in Figure 2.

Thermal gravimetric (TGA) and differential thermal gravimetry (DTG) analysis of the PPA/Al$_2$O$_3$ was investigated by raising its temperature at the rate of 5 °C/min in air up to 800 °C to analyze its thermal decomposition behavior. Fig. 3 shows the TGA/DTG curves of the prepared PPA/Al$_2$O$_3$. Two main stages of weight loss are observed. The first small weight loss at below 100 °C are assigned to the loss of free water and the second weight loss at 179.63 °C is probably due to decomposition or removal of PPA.

The XRD pattern of the PPA/Al$_2$O$_3$ is also presented in Figure 4. Marked peaks are attributed to alumina support.[38] Additional weak and broad peaks are probably related to the

Table 1. N$_2$ adsorption results of PPA/Al$_2$O$_3$ in BET measurements

Sample	Specific surface area (m^2·g^{-1})			Pore diameter (Å)		Pore volume (mL·g^{-1})	
	BET	BJH	DH	BJH	DH	BJH	DH
PPA/Al$_2$O$_3$	131.6	117.0	123.0	21.9	19.7	0.060	0.061
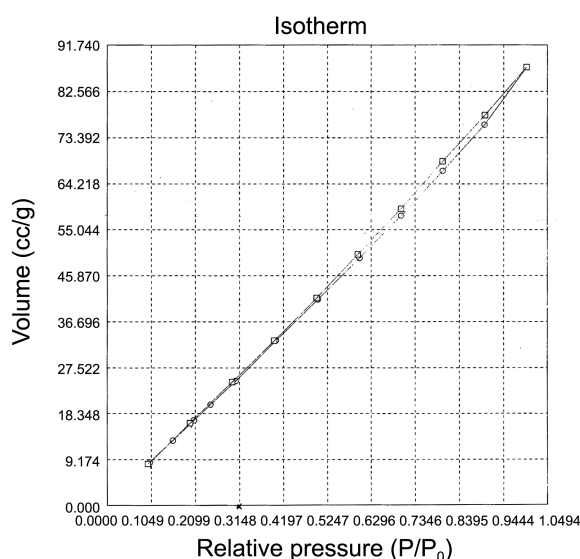
Figure 2. N_2 adsorption-desorption isotherm of PPA/Al_2O_3.
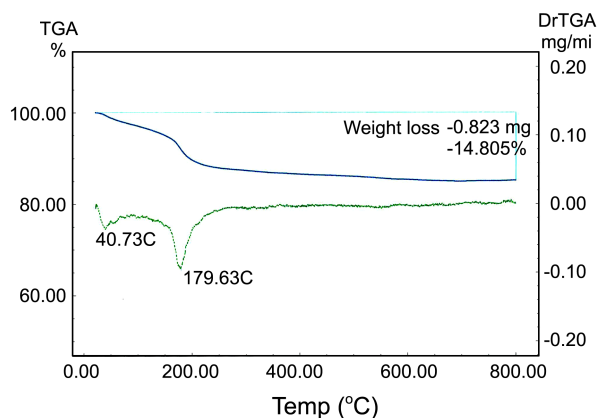

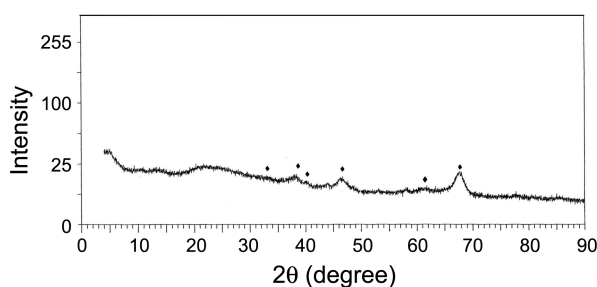**Figure 3.** TGA and DTG curves of PPA/Al_2O_3.

Figure 4. XRD patterns of PPA/Al_2O_3.

formation of PPA/Al_2O_3, suggesting that PPA is highly dispersed on the alumina surface.

Catalytic Performance of PPA/Al₂O₃ in the Synthesis of 14-aryl-14H-dibenzo[a, j]xanthenes. The catalytic activity of PPA/Al_2O_3 as a solid acid supported catalyst was evaluated in the synthesis of 14-aryl-14*H*-dibenzo[*a*, *j*]xanthenes. At first, the synthesis of compound **3d** was selected as a model reaction to determine suitable reaction conditions. The reaction was carried out by heating a mixture of *β*-naphthol (**1**) (2 mmol) and 4-chlorobenzaldehyde (**2d**) (1

Table 2. Effect of PPA/Al_2O_3 amount, solvent and temparature on the model reaction[a]

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Yield (%)[b]
1	None	Solvent-free	120	8 (h)	None
2	0.030	Solvent-free	rt	8 (h)	None
3	0.015	Solvent-free	90	30	65
4	0.015	Solvent-free	120	5	85
5	0.015	Solvent-free	140	5	70
6	0.025	Solvent-free	90	30	73
7	0.025	Solvent-free	120	5	90
8	0.025	Solvent-free	140	5	79
9	0.030	Solvent-free	90	30	78
10	0.030	Solvent-free	120	5	94
11	0.030	Solvent-free	140	5	83
12	0.050	Solvent-free	90	30	69
13	0.050	Solvent-free	120	5	88
14	0.050	Solvent-free	140	5	75
15	0.080	Solvent-free	120	10	82
16	0.100	Solvent-free	120	10	79
17	0.030	H_2O	Reflux	5 (h)	None
18	0.030	EtOH	Reflux	3 (h)	45
19	0.030	CH_3CN	Reflux	2 (h)	56
20	0.030	CH_2Cl_2	Reflux	3 (h)	41
21	0.030	$CHCl_3$	Reflux	4 (h)	38

[a] 2 mmol *β*-naphthol and 1 mmol 4-chlorobenzaldehyde. [b] The yields were calculated based on 4-chlorobenzaldehyde and refer to the pure isolated product.

mmol) in the presence of PPA/Al_2O_3 in different solvents and under solvent-free conditions (Table 2). As can be seen from Table 2, the shortest time and best yield was achieved in solvent-free conditions (entry 10). It was also found that the yield of compound **3d** was strongly affected by the catalyst amount and reaction temperature in solvent-free conditions. No product was obtained in the absence of the catalyst (entry 1) or in the presence of the catalyst at room temperature (entry 2) indicating that the catalyst and temperature are necessary for the reaction. Increasing the amount of the catalyst and reaction temperature up to 0.030 g and 120 °C, respectively, increased the yield of the product **3d**, whereas further increase in both catalyst amount and temperature was found to have an inhibitory effect on formation of the product (entries 5, 8, 11, 14).

Encouraged by this success and in order to evaluate the generality of this model reaction, we extended the reaction of **1** with other aromatic aldehydes (**2a-j**) under the optimized reaction conditions. As shown in Table 3, different aromatic aldehydes reacted successfully with *β*-naphthol in solvent-free conditions, giving the products **3a-j** in high yields and very short reaction times.

Reusability of a catalyst, especially for supported catalysts, is a very important parameter before recommending any catalyst for industrial-scale use. Therefore, in this work, the reusability of PPA/Al_2O_3 was also investigated. For this purpose, the same model reaction was again studied under

Table 3. PPA/Al$_2$O$_3$ catalyzed synthesis of 14-aryl-14*H*-dibenzo-[*a*,*j*]xanthenes **3a-j**[a]

Entry	Ar	Products[b]	Time (min)	Yields (%)[c]	mp (°C) Found	mp (°C) Reported
1	C$_6$H$_5$ **2a**	**3a**	8	90	184-186	182-183[24]
2	3-BrC$_6$H$_4$ **2b**	**3b**	5	92	190-192	190-191[25]
3	4-BrC$_6$H$_4$ **2c**	**3c**	5	94	300-302	295-296[24]
4	4-ClC$_6$H$_4$ **2d**	**3d**	5	94	289-290	287-288[24]
5	4-FC$_6$H$_4$ **2e**	**3e**	6	95	238-240	239-240[24]
6	4-MeOC$_6$H$_4$ **2f**	**3f**	10	86	202-203	203-205[25]
7	4-MeC$_6$H$_4$ **2g**	**3g**	8	90	227-229	227-229[25]
8	2-O$_2$NC$_6$H$_4$ **2h**	**3h**	10	85	213-214	214-215[25]

Table 3. Continued

Entry	Ar	Products[b]	Time (min)	Yields (%)[c]	mp (°C) Found	mp (°C) Reported
9	3-O$_2$NC$_6$H$_4$ **2i**	**3i**	8	89	210-212	210-211[24]
10	4-O$_2$NC$_6$H$_4$ **2j**	**3j**	8	89	310-311	311-312[25]

[a]2 mmol *β*-naphthol, 1 mmol aryl aldehyde, and 0.030 g PPA/Al$_2$O$_3$ at 120 °C under solvent-free conditions. [b]All the products were characterized by IR and ^{1}H NMR spectral data and comparision of their melting points with those of authentic samples. [c]The yields were calculated based on aryl aldehyde and refer to the pure isolated product.

FT-IR spectrum of the recovered catalyst (Fig. 1(d)) was almost identical with that of the fresh catalyst (Fig. 1(c)), indicating that the structure of the catalyst is not destroyed after the reaction.

Conclusion

In conclusion, a new solid acid supported catalyst, PPA/Al$_2$O$_3$, was prepared by impregnation of alumina support by PPA and characterized by FT-IR, BET, TG/DTG and XRD techniques. The catalyst showed high catalytic activity in the synthesis of 14-aryl-14*H*-dibenzo[*a*, *j*]xanthenes by condensation of *β*-naphthol with aryl aldehydes under solvent-free conditions. High yields, short reaction times, recyclability and reusability of the catalyst, easy work-up and absence of any volatile and hazardous organic solvents are just a few of the advantages of this procedure.

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optimized conditions. After the completion of the reaction, the catalyst was recovered according to the procedure mentioned in experimental section and reused for a similar reaction. The catalyst could be reused at least three times with only slight reduction in the catalytic activity (94% for 1st use; 93% for 2nd use; 91% for 3rd use). Furthermore, the

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