DOI 10.5012/bkcs.2011.32.7.2385

Alumina Supported Ammonium Dihydrogenphosphate ($NH_4H_2PO_4/Al_2O_3$): Preparation, Characterization and Its Application as Catalyst in the Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles

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Received April 25, 2011, Accepted May 31, 2011

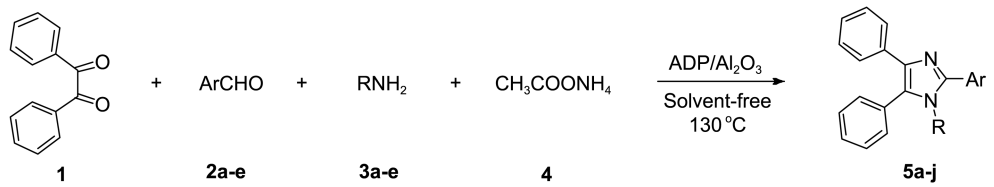
Preparation of ammonium dihydrogenphosphate supported on alumina ($NH_4H_2PO_4/Al_2O_3$) and its primary application as a solid acid supported heterogeneous catalyst to the synthesis of 1,2,4,5-tetrasubstituted imidazoles by a one-pot, four-component condensation of benzil, aromatic aldehydes, primary amines, and ammonium acetate under thermal solvent-free conditions were described. The results showed that the novel catalyst has high activity and the desired products were obtained in high yields. Furthermore, the products could be separated simply from the catalyst, and the catalyst could be recycled and reused with only slight reduction in its catalytic activity. Characterization of the catalyst was performed by FT-IR spectroscopy, the N_2 adsorption/desorption analysis (BET), thermal analysis (TG/DTG), and X-ray diffraction (XRD) techniques.

Key Words : Alumina supported ammonium dihydrogenphosphate, Heterogeneous catalysis, Solvent-free conditions, Tetrasubstituted imidazoles

Introduction

In recent years, heterogeneous catalysts have gained importance due to economic and environmental consideration.[1] The main drawback to the bulk catalyst is its low specific surface area. Therefore, it is important to increase the surface area or even better to increase the number of accessible active sites of the catalyst. In order to reach this objective the catalyst is usually deposited on the surface of a solid support with high surface area and suitable mechanical strength which is able not only to disperse the catalyst, but also to increase its thermal stability and hence the catalyst life. Supported catalysts present a greater number of surface active sites than their bulk components and have been pointed lately as versatile green catalysts for a variety of organic reactions.[2] 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.[3]

As an important member of the five-membered ring heterocycles, imidazole moiety is present in a wide range of naturally occurring molecule.[4] Different substituted imidazoles show variable biological activities such as *anti*-inflammatory,[5] *anti*-allergic,[6] analgesic,[7] antibacterial,[8] and anti-tumor[9] activities. Also, some of them are known as inhibitors of P38 kinase.[10] Recent advances in green chemistry and organometallic catalysis has extended the application of imidazoles as ionic liquids[11] and *N*-heterocyclic carbenes.[12] Despite the availability of a wide variety of synthetic routes toward imidazoles, few studies exist on the synthesis of 1,2,4,5-tetrasubstituted imidazoles. These compounds are generally synthesized in a four-component condensation of 1,2-diketones, aldehydes, primary amines, and ammonium acetate in the presence of several catalysts such as $FeCl_3{\cdot}6H_2O$,[13] ionic liquids,[14] $K_5CoW_{12}O_{40}{\cdot}3H_2O$,[15] $HClO_4$-SiO_2,[16] $InCl_3{\cdot}3H_2O$,[17] NaH_2PO_4,[18] BF_3-SiO_2, $AlCl_3$, and $MgCl_2$.[19] In addition, they can also be accessed by hetero-Cope rearrangement, condensation of a 1,2-diketone with an aryl nitrile and primary amine under microwave irradiation, and *N*-alkylation of trisubstituted imidazoles.[20,21] However, some of these synthetic methods have limitations such as harsh reaction conditions, use of hazardous and often expensive acid catalysts, long reaction times, and moderate yields. Moreover, the synthesis of these compounds is usually carried out in polar solvents such as ethanol, methanol, acetic acid, DMF, and DMSO, leading to complex isolation and recovery procedures. Therefore, the development of simple, efficient, clean, high-yielding, and environmentally friendly approaches using new catalysts for the synthesis of



Scheme 1. Synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by ADP/Al_2O_3.

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[1d-1f,2d,3b,3c,14c,22] we report herein an efficient synthesis of 1,2,4,5-tetrasubstituted imidazoles by a one-pot condensation of benzil, aromatic aldehydes, primary amines, and ammonium acetate using $NH_4H_2PO_4/Al_2O_3$ (ADP/Al_2O_3) as a new solid acid supported catalyst (Scheme 1).

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 ADP/Al_2O_3. The catalyst was prepared by impregnation method. Neutral alumina (Merck, 70-230 mesh, 2.5 g) was added to a solution of ADP (0.6 g) in distilled water (10 mL). The mixture was heated with stirring in the water bath at 40 °C for 30 min to adsorb ADP on surface of alumina. The water was removed with rotary evaporator and the resulting solid powder was dried in vacuo at 120 °C for 3 h. The amount of H^+ in the ADP/Al_2O_3 determined by acid-base titration was 0.5 mmol/g.

General Procedure for the Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles 5a-j Catalyzed by ADP/Al_2O_3. A mixture of benzil **1** (1 mmol), an aromatic aldehyde **2a-e** (1 mmol), a primary amine **3a-e** (1 mmol), ammonium acetate **4** (1 mmol), and ADP/Al_2O_3 (0.15 g) was heated in the oil bath at 130 °C for 1.5-3.0 h. The reaction was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was cooled to room temperature, hot absolute ethanol was added and filtered to remove the catalyst. The catalyst was washed with a small portion of cold water (10 mL), and hot absolute ethanol (10 mL), respectively. The combined filtrate was concentrated by half and allowed to stand at r.t.. The precipitated solid was collected by filtration, dried overnight and recrystallized from absolute ethanol to give compounds **5a-j** in high yields.

Recycling and Reusing of the Catalyst. Due to the fact that the catalyst was insoluble in hot absolute ethanol, it could therefore be recycled by a simple filtration. The separated catalyst was washed with cold water and hot absolute ethanol, dried at 120 °C under vacuum for 3 h and reused in another reaction. The catalyst could be used at least three times with only slight reduction in its catalytic activity.

^{1}H NMR Data for Compounds 5a-j.

1,2,4,5-Tetraphenyl-1*H*-imidazole (5a): ^{1}H NMR ($CDCl_3$, δppm): 7.08 (d, J = 6.4 Hz, 2H, arom-H), 7.18 (dd, J = 7.6, 1.6 Hz, 2H, arom-H), 7.21-7.35 (m, 12H, arom-H), 7.48 (dd, J = 7.4, 1.6 Hz, 2H, arom-H), 7.66 (d, J = 7.2 Hz, 2H, arom-H).

2-(4-Methylphenyl)-1,4,5-triphenyl-1*H*-imidazole (5b): ^{1}H NMR ($CDCl_3$, δppm): 2.35 (s, 3H, CH_3), 7.09 (d, J = 7.8 Hz, 4H, arom-H), 7.17 (d, J = 6.3 Hz, 2H, arom-H), 7.20-7.35 (m, 9H, arom-H), 7.37 (d, J = 8.1 Hz, 2H, arom-H), 7.65 (d, J = 7.3 Hz, 2H, arom-H).

1,2-Bis(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (5c): ^{1}H NMR ($CDCl_3$, δppm): 7.00 (d, J = 8.4 Hz, 2H, arom-H), 7.15 (d, J = 6.8 Hz, 2H, arom-H), 7.20-7.37 (m, 10H, arom-H), 7.39 (d, J = 8.4 Hz, 2H, arom-H), 7.60 (d, J = 7.2 Hz, 2H, arom-H).

1,2-Bis(4-methylphenyl)-4,5-diphenyl-1*H*-imidazole (5d): ^{1}H NMR ($CDCl_3$, δppm): 2.34 (s, 6H, $2CH_3$), 6.95 (d, J = 7.6 Hz, 2H, arom-H), 7.02-7.33 (m, 12H, arom-H), 7.36 (d, J = 7.6 Hz, 2H, arom-H), 7.62 (d, J = 7.6 Hz, 2H, arom-H).

1-Benzyl-2-(4-bromophenyl)-4,5-diphenyl-1*H*-imidazole (5e): ^{1}H NMR ($CDCl_3$, δppm): 5.12 (s, 2H, CH_2), 6.85 (d, J = 6.4 Hz, 2H, arom-H), 7.15-7.45 (m, 11H, arom-H), 7.50-7.65 (m, 6H, arom-H).

1-Benzyl-2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (5f): ^{1}H NMR ($CDCl_3$, dppm): 5.13 (s, 2H, CH_2), 6.82-6.89 (m, 2H, arom-H), 7.16-7.45 (m, 13H, arom-H), 7.62 (t, J = 8.4 Hz, 4H, arom-H).

1-Benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (5g): ^{1}H NMR ($CDCl_3$, δppm): 3.86 (s, 3H, CH_3), 5.12 (s, 2H, CH_2), 6.85 (d, J = 7.3 Hz, 2H, arom-H), 6.95 (d, J = 8.6 Hz, 2H, arom-H), 7.15-7.45 (m, 11H, arom-H), 7.55-7.65 (m, 4H, arom-H).

1-Benzyl-2-(4-methylphenyl)-4,5-diphenyl-1*H*-imidazole (5h): ^{1}H NMR ($CDCl_3$, δppm): 2.41 (s, 3H, CH_3), 5.14 (s, 2H, CH_2), 6.80-6.88 (m, 2H, arom-H), 7.15-7.45 (m, 13H, arom-H), 7.55-7.65 (m, 4H, arom-H).

2-(4-Bromophenyl)-1-methyl-4,5-diphenyl-1*H*-imidazole (5i): ^{1}H NMR ($CDCl_3$, δppm): 3.53 (s, 3H, CH_3), 7.15-7.30 (m, 3H, arom-H), 7.41-7.58 (m, 7H, arom-H), 7.66 (s, 4H, arom-H).

1-Methyl-2-(4-methylphenyl)-4,5-diphenyl-1*H*-imidazole (5j): ^{1}H NMR ($CDCl_3$, δppm): 2.46 (s, 3H, CH_3), 3.53 (s, 3H, CH_3), 7.18 (t, J = 7.3 Hz, 1H, arom-H), 7.25 (t, J = 7.3 Hz, 2H, arom-H), 7.33 (d, J = 7.8 Hz, 2H, arom-H), 7.42-7.55 (m, 5H, arom-H), 7.59 (d, J = 7.6 Hz, 2H, arom-H), 7.67 (d, J = 7.9 Hz, 2H, arom-H).

Results and Discussion

Characterizations of the Catalyst. The catalyst ADP/Al_2O_3 prepared by impregnation of alumina support by ADP was characterized by FT-IR spectroscopy, the N_2 adsorption/desorption analysis (BET), X-ray diffraction (XRD) and thermal analysis (TG/DTG) techniques.

FT-IR spectra of Al_2O_3, ADP and ADP/Al_2O_3 are com-

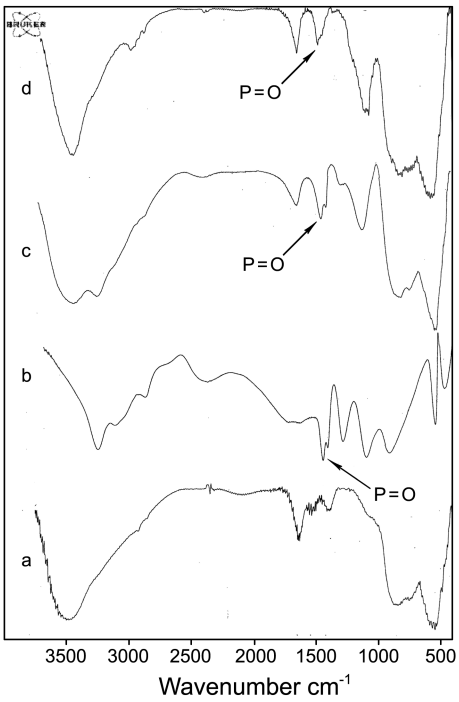


Figure 1. FT-IR spectra of (a) Al_2O_3, (b) ADP, (c) fresh ADP/Al_2O_3, (d) recovered ADP/Al_2O_3.

pared in Figure 1. In the IR spectrum of ADP/Al_2O_3 (Fig. 1c), most of the bands of both Al_2O_3 (Fig. 1a), and ADP (Fig. 1b), with a slight shift for some of them, are observable which indicates ADP has been adsorbed well on the alumina surface. The appearance of absorption in region 1449 cm^{-1} in ADP/Al_2O_3 (Fig. 1c) probably is due to the P=O stretching vibrations of OPO_3H_2 groups that can also be seen in the pure ADP at 1446 cm^{-1} (Fig. 1b).

The specific surface area of ADP/Al_2O_3 measured by the BET method is 87.6 m^2/g. Since the pure alumina has specific surface area of about 130 m^2/g,[23] the decrease in the surface area of ADP/Al_2O_3 may be mainly ascribed to the decrease in the fraction of alumina support due to impregnation by ADP. 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 ADP/Al_2O_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. Figure 3 shows the TGA/DTG curves of the prepared ADP/Al_2O_3. Three main stages of weight loss are observed. The first and second small weight loss at below 100 °C are assigned to the loss of free water and the third weight loss at 693.41 °C is probably due to decomposition of ADP.

The XRD pattern of the ADP/Al_2O_3 is also presented in Figure 4. Marked peaks are attributed to alumina support.[24] Additional weak peaks are probably related to the formation of ADP/Al_2O_3.

Evaluation of Catalytic Activity of ADP/Al_2O_3 in the Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles. The performance of ADP/Al_2O_3 as a solid acid supported catalyst was evaluated in the synthesis of 1,2,4,5-tetrasubstituted

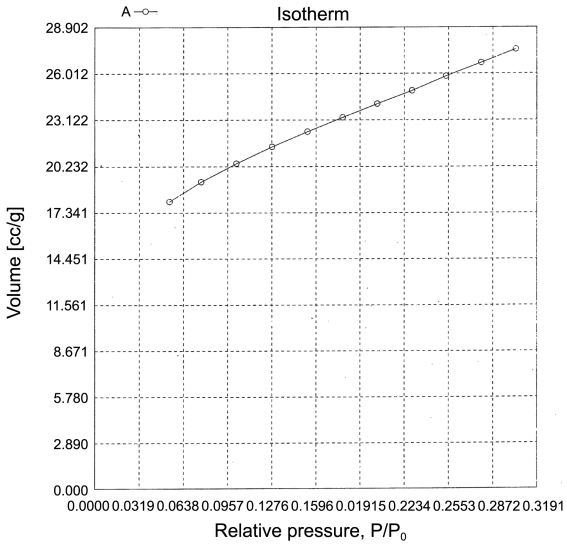


Figure 2. N_2 adsorption-desorption isotherm of ADP/Al_2O_3.

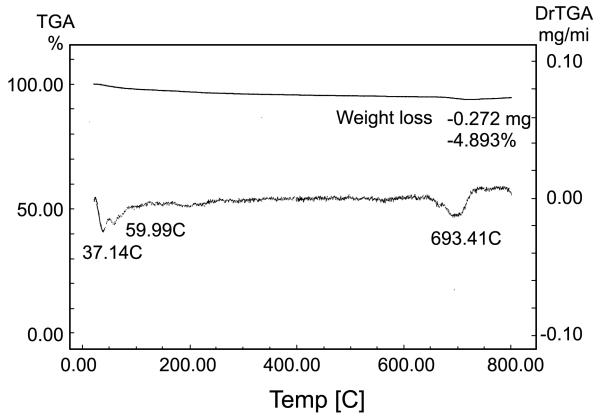


Figure 3. TGA and DTG curves of ADP/Al_2O_3.

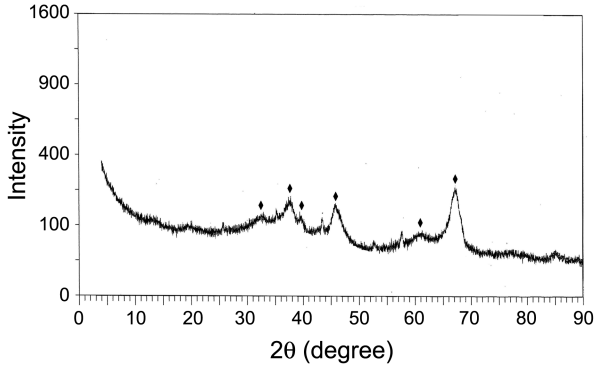


Figure 4. XRD patterns of ADP/Al_2O_3.

imidazoles. At first, the synthesis of compound **5b** was selected as a model reaction to optimize the reaction conditions. The reaction was carried out by heating an equimolar mixture of benzil (**1**) (1 mmol), 4-methylbenzaldehyde (**2b**) (1 mmol), aniline (**3a**) (1 mmol), and ammonium acetate (**4**) (1 mmol) in the presence of ADP/Al_2O_3 in different solvents and under solvent-free conditions (Table 1). As can be seen from Table 1, the shortest time and best yield were achieved

Table 1. Effect of ADP/Al_2O_3 amount, solvent and temparature on the model reaction[a]

Entry	Catalyst (g)	Solvent	T (°C)	Time (h:min)	Yield (%)[b]
1	None	Solvent-free	130	3:00	None
2	0.10	Solvent-free	130	3:00	74
3	0.12	Solvent-free	120	3:30	63
4	0.12	Solvent-free	130	3:00	76
5	0.12	Solvent-free	140	3:00	75
6	0.15	Solvent-free	110	4:00	62
7	0.15	Solvent-free	120	3:00	80
8	0.15	Solvent-free	130	2:30	91
9	0.15	Solvent-free	140	2:30	89
10	0.15	Solvent-free	150	2:30	89
11	0.18	Solvent-free	120	3:00	86
12	0.18	Solvent-free	130	2:30	91
13	0.18	Solvent-free	140	2:30	89
14	0.20	Solvent-free	130	2:30	91
15	0.15	H_2O	Reflux	10:00	Trace
16	0.15	MeOH	Reflux	6:00	40
17	0.15	EtOH	Reflux	6:00	51
18	0.15	CH_2Cl_2	Reflux	10:00	Trace

[a]1 mmol benzil, 1 mmol 4-methylbenzaldehyde, 1 mmol aniline, and 1 mmol ammonium acetate. [b]The yields were calculated based on 4-methylbenzaldehyde and refer to the pure isolated product.

in solvent-free conditions (entry 8). To establish the optimal conditions, a set of experiments varying the amount of the catalyst and temperature were carried out. As can be seen, the efficiency of the reaction is affected mainly by the amount of ADP/Al_2O_3. No product was obtained in the absence of the catalyst (entry 1) indicating that the catalyst is necessary for the reaction. The best result was obtained when the reaction was run at 130 °C in the presence of 0.15 g of ADP/Al_2O_3. An increase in the reaction temperature and amount of the catalyst did not improve the yields significantly.

After optimizing the conditions, we next examined the generality of these conditions to other substrates using several aromatic aldehydes **2a-e** and primary amines **3a-e**. The results are summarized in Table 2. It could be seen that ADP/Al_2O_3 as environmentally benign supported solid acid catalyzed the condensation of **1**, **2a-e**, **3a-e**, and **4** at 130 °C. As indicated in Table 2, in all cases the reaction gives the products in high yields under solvent-free conditions and prevents problems which many associate with solvent use such as cost, handling, safety and pollution.

The principle advantage of the use of heterogeneous solid acid catalysts in organic transformations is their reusability.

Table 2. Synthesis of 1,2,4,5-tetrasubstituted imidazoles **5a-j** using ADP/Al_2O_3 as catalyst[a]

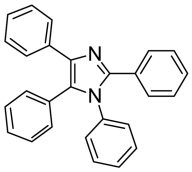
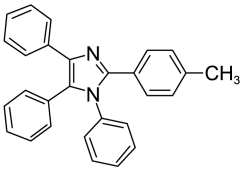
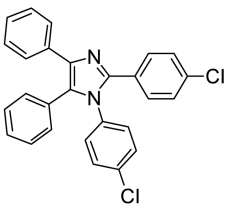
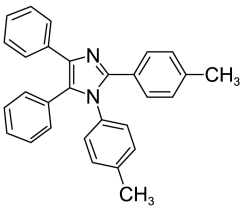
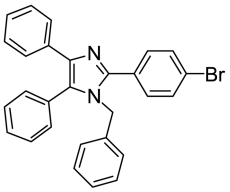
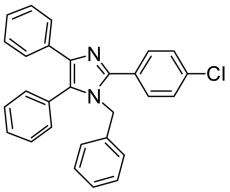
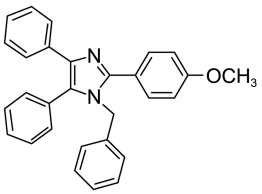
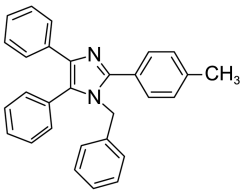
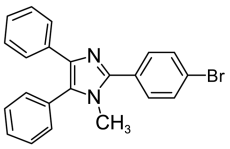
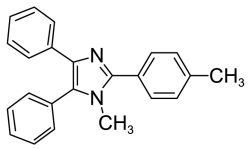
Entry	Ar	R	Products[b]	Time (h:min)	Yields (%)[c]	mp (°C)	
						Found	Reported
1	C_6H_5	C_6H_5		2:15	89	220-222	216-218[19]
	2a	**3a**	**5a**				
2	4-$CH_3C_6H_4$	C_6H_5		2:30	91	189-190	185-188[19]
	2b	**3a**	**5b**				
3	4-ClC_6H_4	4-ClC_6H_4		1:30	88	189-192	187-189[15]
	2c	**3b**	**5c**				
4	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$		2:30	88	193-194	188-191[15]
	2b	**3c**	**5d**				

Table 2. Continued

Entry	Ar	R	Products[b]	Time (h:min)	Yields (%)[c]	mp (°C)	
						Found	Reported
5	4-BrC_6H_4 **2d**	$C_6H_5CH_2$ **3d**	 **5e**	2:00	91	172-175	170-172[16]
6	4-ClC_6H_4 **2c**	$C_6H_5CH_2$ **3d**	 **5f**	2:00	89	165-167	162-165[19]
7	4-$CH_3OC_6H_4$ **2e**	$C_6H_5CH_2$ **3d**	 **5g**	2:15	87	161-162	157-160[16]
8	4-$CH_3C_6H_4$ **2b**	$C_6H_5CH_2$ **3d**	 **5h**	2:30	89	166-168	165-166[19]
9	4-BrC_6H_4 **2d**	CH_3 **3e**	 **5i**	2:30	80	202-203	201-202[13]
10	4-$CH_3C_6H_4$ **2b**	CH_3 **3e**	 **5j**	3:00	85	224-226	221-223[13]

[a]1 mmol benzil, 1 mmol aromatic aldehyde, 1 mmol primary amine, 1 mmol ammonium acetate, and 0.15 g ADP/Al_2O_3 at 130 °C under solvent-free conditions. [b]All the products were characterized by IR and ^1H NMR spectral data and comparision of their melting points with those of authentic samples. [c]The yields were calculated based on aromatic aldehyde and refer to the pure isolated product.

Hence, we decide to study the catalytic activity of recycled ADP/Al_2O_3 in the synthesis of compound **5b**. ADP/Al_2O_3 being insoluble in most of the common organic solvents, upon completion of the reaction, the reaction mixture was cooled to room temperature, and hot absolute ethanol was added. The catalyst was recovered by simple filtration, washed with cold water and hot absolute ethanol, dried at 120 °C in vacuo for 3 h and reused in a similar reaction. The

catalyst could be reused at least three times with only slight reduction in the catalytic activity (91% for 1st use; 89% for 2nd use; 86% for 3rd use). Furthermore, retention of the structure of the catalyst was confirmed by comparing the FT-IR spectrum of the recovered catalyst (Fig. 1d) with that of the fresh catalyst (Fig. 1c) for model reaction. As shown, both spectra are almost identical.

Conclusion

In summary, a new solid acid supported catalyst, ADP/Al_2O_3, was prepared by impregnation of alumina support by ADP and characterized by FT-IR, BET, TG/DTG and XRD techniques. The catalyst showed high catalytic activity in the synthesis of 1,2,4,5-tetrasubstituted imidazoles by condensation of benzil, aromatic aldehydes, primary amines, and ammonium acetate under solvent-free conditions. Some attractive features of this protocol are high yields, simple procedure, the elimination of organic solvents and toxic reagents, and recyclability and reusability of the catalyst.

Acknowledgments. The authors are thankful to Islamic Azad University, Mashhad Branch for financial support.

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