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Research Paper

Fly Ash Mediated Acylation of Phenols in Solvent Free Conditions under Microwave Irradiation

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Abstract: Acylation of phenols was carried out in presence of solid acid fly ash catalyst under microwave irradiation in solvent free conditions. An efficient, simple acylation reaction affords good yields of the product and the catalyst could be easily recovered and recycled.

Introduction

Esterification of alcohols and phenols by employing activated acetic acid is termed as acylation. Anhydrides are the most reactive derivatives of carboxylic acids after the acid chlorides used in acylation. Phenyl acetate ester prepared industrially by using acetic anhydride, is an important intermediate in the synthesis of acetaminophen. Aspirin or acetylsalicylic acid is prepared in large scale by acylation reaction of salicylic acid with acetic anhydride by using H_2SO_4 , H_3PO_4 as a catalyst. It is also used in the production of cellulose acetate by the esterification of cellulose or cotton. The acylation employing acetic anhydride is fast

and irreversible. Nevertheless, at the end of the acylation reaction, the acid catalyst has to be neutralized in order to isolate the product. The replacement of traditional homogenous Lewis and Bronsted acid catalysts by heterogeneous ones, e.g. solid acid catalysts [1] constitute a more environmentally friendly alternative to the organic reactions. These solid catalysts perform well due to high surface area that reduces the reaction time and it avoids the onset of reversible reaction. Advantageously, the acid sensitive groups are found to have tolerance to such solid acid catalysts. Operationally, these catalysts are easy to handle as post reaction work up may simply involve filtration of the catalyst from the heterogeneous mixture of the

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reaction mass. The filtered catalyst can be recovered and reused.

Several metal oxides and supported systems including YO_2 - ZrO_2 [2], ZnO [3], transition metal oxides [4], montmorillonites [5], HClO_4 - SiO_2 [6], H_2SO_4 - SiO_2 [7], $\text{AlPW}_{12}\text{O}_{40}$ [8], Zeolites [9], Nafion -H [10], HbF_4 - SiO_2 [11], KFAI_2O_3 [12], MoO_3 - Al_2O_3 [13], NaHSO_4 - SiO_2 [14], sulphated zirconia [15], $(\text{NH}_4)_2\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$ [16], [TMBSA][HSO_4] ionic liquid [17], silica bonded cobalt II [18], Silica bonded N propyl sulfamic acid S- propyl sulphuric acid [19], $\text{H}_6\text{GeW}_{10}\text{V}_2\text{O}_{40} \cdot 22\text{H}_2\text{O}$ [20] and Zn dust [21] have been used as heterogeneous catalysts for the acylation of phenols.

Microwave mediated solvent-free synthesis of organic compounds involving easily separable solid catalysts has attracted notable interest and offers a clean, economical and environmentally-safe protocols [22].

Materials and Methods

Fly ash is the solid waste residue produced from coal, oil, and biomass combustion. In the past few decades, more and more research has been devoted to explore the applications of fly ash in heterogeneous catalysis. It is a silico-aluminate material consisting of SiO_2 , Al_2O_3 , and Fe_2O_3 as the major constituents and varying amount of CaO , MgO , SO_3^- with unburned carbon. Besides these, some minor elements such as Hg, As, Ge, Ga, and traces of heavy metals (Cr, Co, Cu, Pb, Mn, Ni, Zn) & other rare earth metals may also be present in fly ash [23].

The catalytic role of activated fly ash for different reactions such as oxidation [24, 25], chlorination [26] and condensation of

short chain olefins [27] is well documented in the literature. Fly ash was also used as solid support in the synthesis of 2-mercaptobenzothiazole derivatives under microwave irradiation [28]. Solvent free alkylation and acylation of thymol and geraniol using fly ash as solid support is reported [29].

Recently, solid acid catalyst synthesized from fly ash has been used as a catalyst for acylation of salicylic acid under thermal conditions [30].

Herein we attempted microwave assisted acylations of phenolic substrates in presence of fly ash.

Fly ash was obtained from Khaparkheda power plant, District Nagpur, Maharashtra state, India. The collected fly ash has the following composition: SiO_2 , 50-54; Al_2O_3 , 22-25; Fe_2O_3 , 2-5; MgO , 0.5-2.5 and others (MnO_2 , CaO , P_2O_5 , TiO_2 , SO_3^- , Na_2O , K_2O , 0.002-2.5%) .

The irradiation with 300 W in the MW (Model MO9621, 2450 MHz, 900W) was employed.

Fly ash was riddled in a sieve to remove any coarser and foreign particles. The particle size distribution was found to be between 40-60 μm .

The solid acid activated fly ash catalyst was synthesized as mentioned in the literature [30]. The acylations were carried out with the substrate to catalyst ratio as 10: 1. The catalyst which was used in the reaction mixture was recovered by filtration and regenerated for next cycle.

Initially, two substrates were subjected to acylation reactions in the presence of three types of catalysts. Fly ash without any

activation (Type I), thermally activated fly ash (Type II) & chemically activated fly ash (Type III) were used as catalysts for acylation reaction of phenolic substrates, 2a & 2b (Table No 1). Fly ash obtained from the thermal power plant was used as such without any pre-treatment as Type I catalyst. Type II fly ash catalyst was obtained by calcining the fly ash at 600^oC for 4 h. The synthesis of Type III fly ash catalyst involves a chemical treatment followed by thermal treatment. Fly ash and concentrated H₂SO₄ acid in 1:2 weight ratios were stirred in a round bottom flask equipped with a mechanical stirrer for five days at 110^oC. The dark pulp obtained was washed with distilled water to remove leached compounds and dried at 110^oC for 24 h. The obtained chemically activated fly ash (Type III) was thermally stabilized by calcining at 600^oC for 4 h without any agitation.

Results and Discussion

Chemically activated fly ash solid catalyst (Type III) gave better results as compared to Type I & Type II catalysts. The results indicate that conversion as high as a 98% of acylated product was achieved by using Type III catalyst as shown in Table 1.

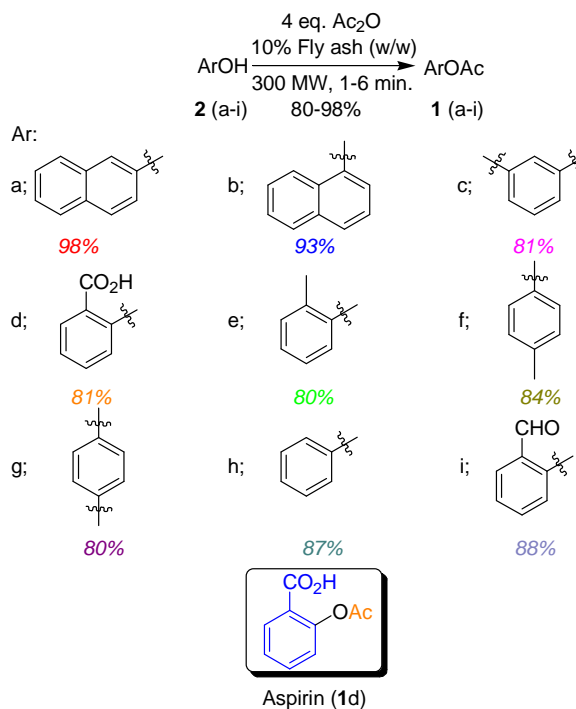
The scope of fly ash catalysed acylations of phenolic compounds under microwave irradiation was then explored with Type III catalyst. The results in Table 2 suggest generality of this method and the efficiency of fly ash as a catalyst. The results also indicate the reduction of reaction time as compared to acylation reaction conducted under thermal conditions [30].

We have examined the recovery and reuse of the activated fly ash in the acylation of β-naphthol to get 2-naphthyl acetate and found that the yields of the products in the second and third use of the catalyst were almost same as that in the first run. In every case,

fly ash catalyst was recovered by filtration, washing with acetone and dried in oven at 110^oC for 1 h.

Table 1: Acylation of phenols with Type I, Type II & Type III fly ash

Substrate	Fly ash type					
	Type I		Type II		Type III	
	Time (Sec)	Yield (%)	Time (Sec)	Yield (%)	Time (Sec)	Yield (%)
2a	295	96	280	98	250	98
2b	290	90	255	92	230	93



Scheme 1: Acylation of phenols

Table 2: Solvent free Acylation of phenols with acetic anhydride in presence of Type III fly ash under microwave irradiation

S. N.	SM	Product	(^o C) ^b /Sec	Yield (%)	MP or BP (^o C)
1	2a	1a	118/250	98	70 /72 ^c
2	2b	1b	118/230	93	48/49 ^c
3	2c	1c	124/80	81	Liq/146 ^{a*}
4	2d	1d	122/150	81	133/135 ^c
5	2e	1e	120/230	80	Liq/ 208 ^a

6	2f	1f	100/30	84	Liq/212 ^a
7	2g	1g	122/320	80	122/124 ^c
8	2h	1h	126/120	87	Liq/196 ^a
9	2i	1i	120/230	88	38/39 ^c

^a Aldrich catalog handbook of fine chemicals **2000-2001**; ^b The reaction temperature was measured by immersing a glass thermometer in the reaction mixture at the end of exposure to microwave irradiation and gives an approximate temperature range * Boiling point at 12 mm Hg. ^c Ref [31]

Experimental Section

Acylation of various phenols as shown in Scheme 1 have been performed by mixing phenolic substrate (1 mmol), acetic anhydride (4 mmol) & Type III fly ash in a 50 mL borosil beaker.

The reaction mixture was irradiated in a microwave oven at 300 W for specified time as mentioned in the Table 2. The reactions were monitored on TLC by comparison with authentic samples. Melting points were taken in open capillaries using paraffin baths and are uncorrected. The catalyst was activated at 450 °C in static air prior to the reaction for 2 h. The crude product was subjected to silica gel column chromatography using 5% EtOAc in light petroleum ether as eluent to get corresponding acylated product 80-98 % yields (Table 2).

The structure of the product was confirmed by ¹H NMR, IR and by comparison with the authentic samples obtained commercially or prepared by reported methods.

Synthesis of 2-naphthyl acetate (Table No 2, Entry 1)

To a mixture of β naphthol (1 mmol) & acetic anhydride (4 mmol) in a 50 mL borosil beaker, activated fly ash (naphthol to

catalyst weight ratio 10:1) was added. The reaction mixture was stirred properly with the help of a glass rod (<1min.) and then irradiated in a microwave oven at 300 W for 4 min. The progress of the reaction was monitored by TLC. The catalyst was removed by filtration and the reaction mass was added in chilled water to get the crude product. The crude product was subjected to silica gel column chromatography using 5% EtOAc in light petroleum ether as eluent to get 2-naphthyl acetate (98%). IR (KBr) 1755 cm⁻¹, ¹H NMR (CDCl₃), δ 2.30 (s, 3H), 7.24 (d, *J* = 8.85 Hz, 1H), 7.44 (m, 2H), 7.56 (s, 1H), 7.78 (m, 3H), ¹³C NMR (CDCl₃), δ 21.19, 118.53, 121.13, 125.71, 126.56, 127.64, 127.76, 129.41, 137.47, 133.75, 148.33, 169.65.

Conclusion

In conclusion, we have demonstrated an efficient and simple alternative for the acylation reactions of phenols using microwave irradiation under solvent free conditions. The Type III catalyst (Chemically activated) was found to be a slightly better catalyst than Type I & Type II catalysts. The process offered a dramatic reduction of reaction time. The attractive features of this process are the mild reaction conditions, high conversions, cleaner reaction profiles, operational simplicity and use of an easily and abundantly available fly ash, an industrial waste pollutant as a recyclable catalyst.

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