Friedel–Crafts acylation of aromatic compounds

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Abstract

An efficient method for the Friedel–Crafts acylation of a wide range of aromatic compounds in good to excellent yields under solvent-free conditions, using iron zirconium phosphate (ZPFe) was investigated. The catalyst is easy to prepare and shows interesting catalytic properties. The catalyst was characterized by some instrumental techniques such as XRD, ICP-OES, SEM and TEM. A wide variety of benzene derivatives reacted easily with benzoyl chloride and some of its derivatives to afford the corresponding aromatic ketones in clean and good yields with the para isomer predominating typically using 3mol% of catalyst. The use of inexpensive materials, simple and clean work-up, short reaction times in most cases and good yields are the main advantages of this method. This work introduces a new application of this catalyst, not described in the literature until now. Also, the catalyst can be recovered and reused for three times without a significant loss in its activity and selectivity.

Keywords: Iron zirconium phosphate; nanoparticles; acylation; solvent-free; solid catalyst

1. Introduction

Friedel–Crafts acylation of aromatic compounds is one of the most important and practical methods to prepare aromatic ketones. The resulting diaryl ketones are important chemical intermediates for the synthesis of a wide range of compounds such as pharmaceuticals, fragrances, flavors, dyes and agrochemicals (Cornelis et al., 1993; Effenberger et al., 1996). This is an electrophilic acylation of aromatic compounds with acid chlorides or acid anhydrides, which is traditionally catalyzed by Lewis acids, such as $AlCl_3$, BF_3, $SbCl_5$, $FeCl_3$, $ZnCl_2$, $SnCl_4$, $TiCl_4$ or strong protonic acids, such as H_2SO_4, HF (Barrett et al., 2002; Bensari and Zaveri, 2003; Chapman et al., 2001; Leon Bradlow and Vanderwerf, 1947; Paul et al., 2003). The major drawbacks of these catalysts are that they are hazardous, corrosive, non-recoverable and, usually, more than stoichiometric amounts of catalysts are required. In order to overcome these problems, various catalysts have been reported (Bartoli et al., 2002; Effenberger et al., 2000; Firouzabadi et al., 2004; Hajipour et al., 2009; Matsuo et al., 2000; Répichet et al., 2003; Sartori and Maggi, 2006; Zarei et al., 2008).

Zirconium phosphate (ZP) is an important inorganic material which has been prepared in both amorphous and crystalline forms by various methods (Clearfield and Stynes, 1964; Hajipour and Karimi, 2014; Sun et al., 2005; Sun et al., 2007). The layered structure of ZP consists of Zr^{+4} ions which are connected through the oxygen atoms of phosphate groups from above and below. Each zirconium is octahedrally coordinated by six oxygens of six different phosphate groups. The arrangement of these groups creates six-sided cages, one for each Zr atom (Clearfield and Stynes, 1964; Hajipour and Karimi, 2014). ZP is drawing increasing attention as a low cost, efficient and reusable compound which is used in many fields (Chaudhari and Kumar, 2005; Kamiya et al., 2004; Saxena et al., 2013; Mishra et al., 2006). It is an important ion exchanger (Mishra et al., 2006; Ahrland et al., 1970; Bhattacharyya and Basu, 1978; Chekhomova and Cherednichenko, 1998; Moosavi et al., 2009) due to its extreme insolubility in water, high thermal stability and resistance to radiation and abrasion (Kamiya et al., 2004). The H^+ of the P–OH being the exchangeable sites can be exchanged for other ions with proper enlargement of the interlayer distance. Exchange of various cations, divalent or trivalent, such as Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+} and Zn^{2+}, into layers of ZP has already been achieved (Alberti et al., 1977; Alberti et al., 1996; Borgo and Gushikem, 2002;

Cai et al., 2012; Clearfield, 1988; Dai et al., 2012; Pan et al., 2007; Yang et al., 2011; Zhang et al., 2008). Moreover, ZP showed antibacterial activity when Zn^{2+} and Ce^{3+} were loaded into it (Cai et al., 2012; Dai et al., 2012; Yang et al., 2011). Also, there are some reports about catalytic activities of these ion exchanged materials (Gawande et al., 2005; Khare and Chokhare, 2012; Preetha and Janardanan, 2011; Pylinina and Mikhalenko, 2011; Pylinina and Mikhalenko, 2013; Wang et al., 2013).

Our research group is interested in the field of heterogeneous catalysts (Hajipour et al., 2014; Hajipour and Karimi, 2014; Hajipour and Karimi, 2014; Hajipour and Karimi, 2014), especially Friedel–Crafts acylation and acetylation of aromatic compounds (Hajipour et al., 2009; Hajipour et al., 2009). Herein, we report preparation and characterization of iron zirconium phosphate (ZPFe) as an efficient, convenient and recoverable heterogeneous solid catalyst for acylation of some aromatic compounds to the corresponding aryl ketones, which were characterized by ICP-OES, XRD, SEM and TEM.

2. Experimental

All Chemicals and solvents were purchased from Merck Chemical Company and used without further purification. All yields refer to isolated products after purification. All products were characterized by comparison with authentic samples and by spectroscopy data FT-IR and ^{1}H NMR analysis. ^{1}H NMR spectra were recorded on a Bruker-Avance AQS 400 MHz spectrometer. The spectra were measured in $CDCl_3$ unless otherwise stated, relative to TMS (0.00 ppm).

2.1. Catalyst synthesis

The detailed procedure for the preparation of catalyst can be found in the literature (Sun et al., 2005; Sun et al., 2007). It has been prepared with some modifications. ZP was prepared as follows: typically, 5 g $ZrOCl_2.8H_2O$ was refluxed with 50 ml of 12 M H_3PO_4 at 100 °C for 24 h. The obtained precipitate was filtered off and washed with 0.1 M H_3PO_4 until free of chloride ion. Finally, the solid was washed with distilled water several times until neutral pH and dried in an oven at 110 °C for 24 h. The final product was ground into fine powders and confirmed by XRD (Fig.1). The ZPFe was prepared through an ion-exchange reaction (Allulli et al., 1976; Khare and Chokhare, 2011). 3 g of ZP was dispersed into 50 ml deionized water at 50°C. 100 ml of $Fe(AcO)_3$ solution (0.1 N) (excess amount of Fe^{3+}) was added to the dispersed solution of ZP and refluxed for 4 days. It is noticeable that acetate ion effectively acts as a base to keep the hydrogen ion concentration in solution low enough to achieve high loadings (Clearfield and Kalnins, 1978). A complete exchange between the

cations and the hydrogen of the P-OH groups cannot be achieved in less than 3 days or at a temperature below 80 °C (Yang et al., 2011). The slurry was filtered hot and the obtained light yellow solid was washed with distilled water until no Fe^{3+} in washing solution was detected (the filtrate was colorless) After that, the product was dried at 100 °C overnight and calcined at 600 °C for 5h. The final pale product, iron zirconium phosphate, $Fe_{1/3}[Zr_2(PO_4)_3]$, was denoted as ZPFe (Scheme 1).
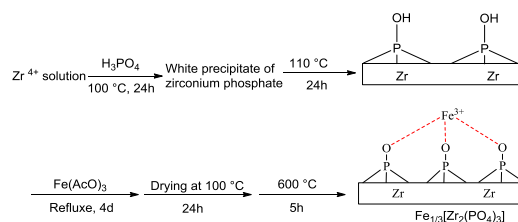
Scheme 1. Summarized procedure for ZPFe preparation

2.2. Acylation of Aromatic Compounds

The acylation reaction was carried out in a round bottom flask, equipped with a magnetic stirrer and water condenser under solvent-free condition. ZPFe (3 mol%) was added to a mixture of a benzoyl chloride (10 mmoL) and an aromatic compound (10 mmoL). The reaction mixture was stirred for the appropriate reaction times at 80°C. After completion of the reaction (monitored by thin-layer chromatography, TLC), the mixture was diluted with Et_2O and filtered. The organic layer was washed with 10% $NaHCO_3$ solution and then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the product purified by column chromatography on silica gel to give the corresponding pure aryl ketone.

3. Results and discussion

The chemical composition of ZPFe obtained at different stages of the synthesis of catalyst (before and after catalytic reaction), was checked by ICP-OES (PerkinElmer icp-oes 7300 dv spectrometer) and the results are shown in Table 1. It was compared with earlier results (Gawande et al., 2005; Khare and Chokhare, 2011; Costantino et al., 2001). There is a negligible leach of iron ions into the reaction media after reaction till the 4th cycle.

Table 1. Element contents of iron zirconium phosphates (atm.%)

Samples	Fe	O	Zr	P
ZP	-	72.1	11.3	16.6
ZPFe	3.3	71.0	10.7	15.0
ZPFe[a]	3.2	71.5	10.5	14.8
ZPFe[b]	1.1	72.1	11.0	15.8

[a] After run 1
[b] After run 4

The crystallinity of ZPFe was measured by X-ray powder diffractometer (Philips X'pert). The samples were scanned in the 2θ range of 5–40°, Fig. 1. It Some characteristic reflections in the 2θ range of 5–40° are shown that have fair agreements with the results in the literature (Khare and Chokhare, 2011; Costantino et al., 2001; Gobechiya et al., 2004; Sun et al., 2004). The diffraction peak of ZP at 2θ ~ 12 ° indicates a spacing of 7.6 Å for the planes and the reported refined crystal structure of ZP (Sun et al., 2005; Sun et al., 2007).
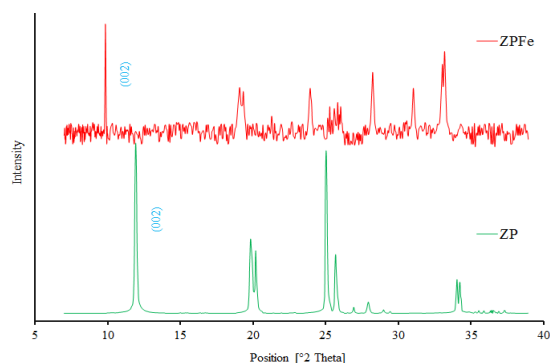
Fig. 1. XRD patterns of powder ZP (down), ZPFe (up)

It is well known that the ion radii of Fe^{3+} (0.64 Å) and even hydrated ionic radius of Fe^{3+} (3.9 Å) (Kielland, 1937; Shannon, 1976) are smaller than basal spacing of ZrP (7.6 Å). Therefore, Fe^{3+} was inserted into the interlayer of ZP and increased basal spacing of the modified ZP after the exchange. Fig. 1 represents the diffraction peak at 2θ = 9.8° for ZPFe. Also, an increase in d-spacing in the fully exchanged ZPFe with respect to that of its precursor ZP (9.3 vs. 7.6 Å) is evident. The shift of 1.7 Å in the d-spacing is due to the intercalation of Fe^{3+}. It is clearly demonstrated that Fe^{3+} intercalated into the interlayer of ZP. Therefore, from the above data, formation of ZPFe was concluded.
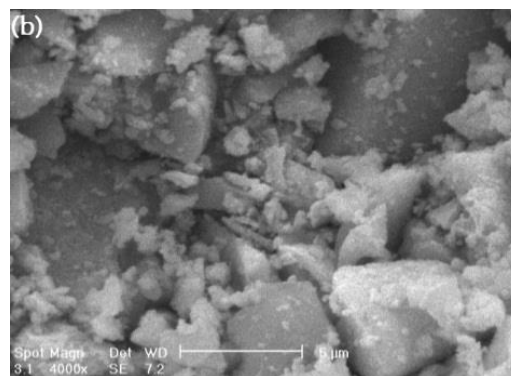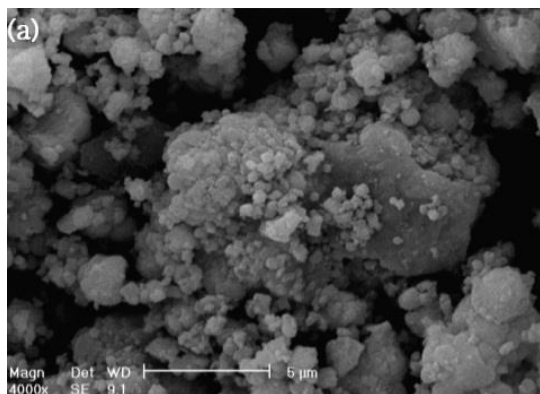
Fig. 2. SEM images of regular morphology of prepared ZP (a) and ZPFe (b).

The morphology of the samples was investigated using SEM (Philips XL) (Fig. 2). The surface morphology of the ZP and ZPFe was studied by SEM (Khare and Chokhare, 2011; Sun et al., 2004), (Fig. 2). The SEM micrograph of ZP, Fig. 2a., shows the hexagonal plates, the disks of which had well-defined shapes with very smooth surface. Fig. 2b. shows the SEM image of ZPFe which is much less ordered in comparison to that of ZP. Some aggregation of ZPFe particles is shown in both sheets and spherical shapes, where its particles are mostly conglomerate with uneven shape and size. Fig. 3 represents the TEM (CENTRA 100, Zeiss) images of ZP and ZPFe. The TEM images of ZPFe, Fig 3a and 3b (different magnification), show that the ZPFe retains the original morphology of the ZP, and a size of ~ 150 nm with clear crystal habit was observed. They show nanoparticles, which are on the smooth surface of the ZP with different sizes. The observable existence of metallic crystal nanoparticle indicates that agglomeration of iron deposited on the surface of the ZP. Almost the same observations were reported for zinc and cerium zirconium phosphate earlier (Cai et al., 2012; Dai et al., 2012).
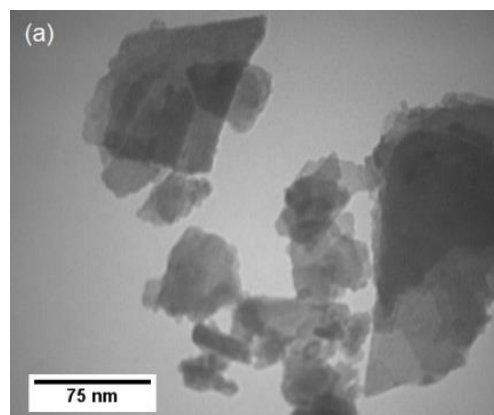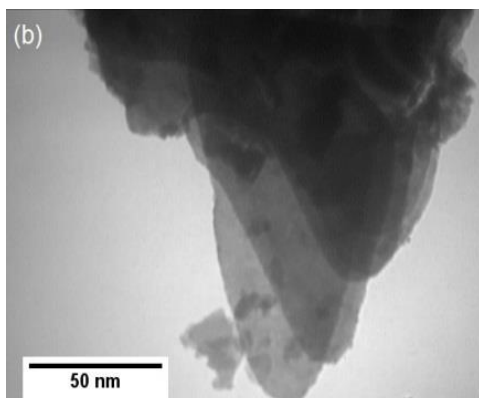
Fig. 3. TEM images of regular morphology of prepared ZPFe (different magnification)

The acylation reactions were carried out by heating a stirring mixture of the benzoyl chlorides such as p-methoxybenzoyl chloride, p-nitrobenzoyl chloride and p-fluorobenzoyl chloride with corresponding aromatic compounds such as mesitylene, indole, toluene, o-xylene, m-xylene, p-bromoanisole and benzene under solvent-free conditions. The products were isolated by simple filtration of the reaction mixture and then by the usual work-up. Different structures of aromatic rings underwent acylation with benzoyl chlorides. These reaction conditions were successfully applied for the preparation of different aryl ketones from electron-rich and electron-poor aromatic compounds. The results are presented in Table 2. The reactions are remarkably clean, convenient, and no chromatographic separation is necessary to get the spectra-pure compounds.
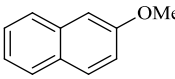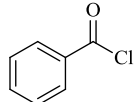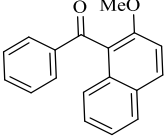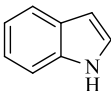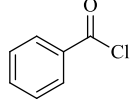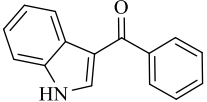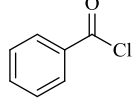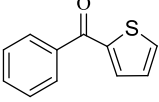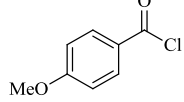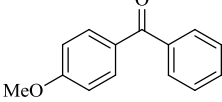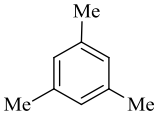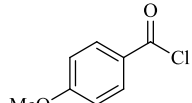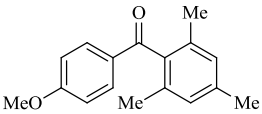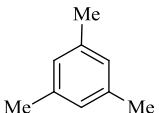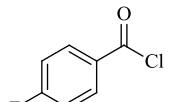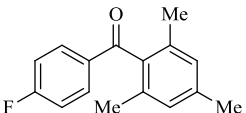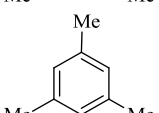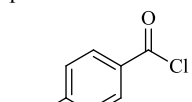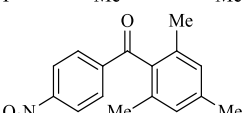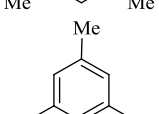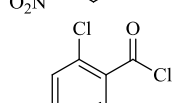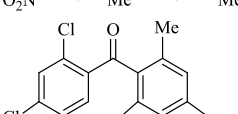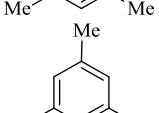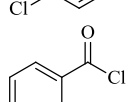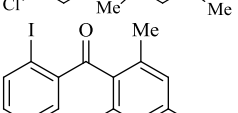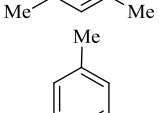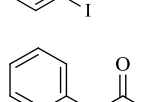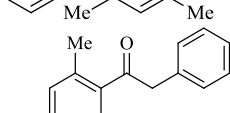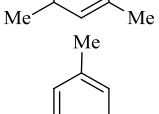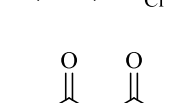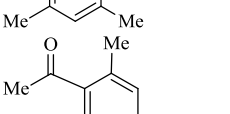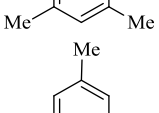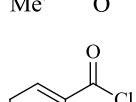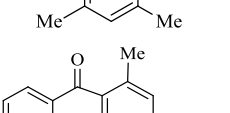
The acetylation rate is therefore primarily controlled by electronic factors, activating or deactivating substituents on the aromatic ring having a strong influence on the reactivity of the substrates. Conversely, in all cases, the reactivity of poorly activated or nonactivated arenes (as fluorobenezene) was very low and of scarce practical relevance, at least under the conditions tested here. The presence of Cl and Br as strong electron-withdrawing groups on the aromatic ring reduced drastically the yield of the acylation reaction (Table 2, entries 10, 11). Also, the deactivated nitrobenzene did not react. The benzoylation of activated aromatics yielded the ketones in excellent yields (Table 2, entries 2-8). The acylation of alkyl-substituted benzenes such as toluene is more difficult, and some of the methods reported in the literature are not applied to this substrate or gave poor yields of ketone (Arai et al., 2005; Jang et al., 2006). Under our catalytic conditions, acylation of toluene, o-xylene and p-xylene gave the corresponding ketones in moderate yields (Table 2, entries 2–4), and the acylation of toluene afforded a mixture of para/ortho-

regioisomers with a high para-selectivity (Table 2, entry 2). By using this reagent, acylation occurs at the para position with high selectivity. However, in cases where the para position is blocked (Table 2, entries 9,11), the acyl group introduces ortho to the substituted groups on aromatic rings. This procedure is also good enough for the acylation of heterocyclic aromatic compounds such as indole and thiophene (Table 2, entries 13,14), as well as polycyclic aromatic hydrocarbons such as 2-methoxynaphthalene (Table 2, entries 12), producing the corresponding acylated products in good yields. Also, to establish the generality and applicability of this method, the Friedel–Crafts acylation of mesitylene with different acyl chlorides was investigated (Table 2, entries 15-21). The activities of the ZPFe in the acylation of aromatics with benzoyl chloride can be correlated to their predominant Lewis acidity (Fe^{3+}) that is critical for the activity in this reaction. ^{1}H NMR and IR spectral data for products are presented in supplementary data.

An important feature of this procedure is the survival of a variety of functional groups such as ethers. Also, to evaluate the role of our catalyst, the reaction was performed in the absence of any catalyst (Table 2, entry 23), no significant amount of product was detected. In order to examine the recyclability of the catalyst, spent ZPFe was recovered from the reaction media and re-used. For recycling, after first use, the catalyst was separated from the reaction mixture by centrifuge, washed with ethanol successively, then with water, dried at 110°C for 2 h and finally activates at 400°C for 2 h. Spent ZPFe gave a similar yield of products as the fresh catalyst till the 4th cycle. The regenerated catalyst was characterized for its chemical composition by elemental analysis after each reaction (Table 1). No significant changes in composition of catalyst were observed after regeneration till the 4th cycle.

Table 2. Acylation of aromatic compounds with acyls in the presence of ZPFe under solvent-free conditions
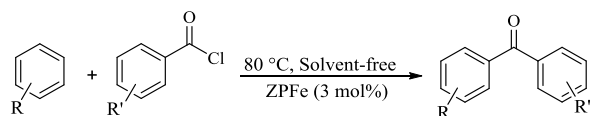
R: CH$_3$, (CH$_3$)$_2$CH, OH, OCH$_3$, Br, Cl
R': F, Cl, I, OCH$_3$, NO$_2$

Entry	Aromatics	Acylating reagent	Product	Time (min)	ZPFe [a]
1				90	80
2				60	87 (90:10)[b]
3				45	95
4				45	95 (92:8)[b]
5				30	>99
6				45	83
7				30	>99 (90:10)[b]
8				30	97
9				60	95
10				120	70
11				150	70

#	Substrate	Acyl	Product	Time (min)	Yield (%)
12	2-methoxynaphthalene	benzoyl chloride	(1-benzoyl-2-methoxynaphthalene)	30	97
13	indole	benzoyl chloride	(3-benzoylindole)	15	>99
14	thiophene	benzoyl chloride	(2-benzoylthiophene)	120	70
15	benzene	4-methoxybenzoyl chloride	(4-methoxybenzophenone)	90	92
16	mesitylene	4-methoxybenzoyl chloride	product	30	>99
17	mesitylene	4-fluorobenzoyl chloride	product	45	21
18	mesitylene	4-nitrobenzoyl chloride	product	60	10
19	mesitylene	2,4-dichlorobenzoyl chloride	product	60	78
20	mesitylene	2-iodobenzoyl chloride	product	60	>99
21	mesitylene	phenylacetyl chloride	product	30	>99
22	mesitylene	acetic anhydride	product	30	95
23	3,5-dimethyl (xylene)	benzoyl chloride	product	120	-

[a]Yields based on the starting acyl, refers to the isolated pure products
[b]Para:ortho ratio

Table 3. Catalyst re-used under the optimum reaction conditions for acylation of mesitylene

Substrate [a]	Fresh	run 1	run 2	run 3	run 4
Mesitylene	99	97	96	93	81

[a]Reaction conditions: mesitylene (10 mmol), benzoyl chloride (10 mmol), catalyst (3 mol%), 80 °C and 30 min

Regenerated catalyst re-used for acylation of mesitylene with benzoyl chloride, the results are summarized in Table 3.

4. Conclusions

ZPFe is inexpensive, easily available, noncorrosive, and an environmentally benign compound. In this work, we have reported a simple and efficient procedure for the preparation of aryl ketones in good yields and short reaction times. The notable advantages of this methodology are the use of a wide variety of benzoyl chloride and aromatic compounds, generally, high regioselectivity, availability of reactants and easy work-up as a result of the heterogeneous conditions.

Acknowledgments

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