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$K_2FeZrP_3O_{12}$ as an efficient catalyst for Friedel–Crafts benzylation under solvent-free conditions

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Abstract: $K_2FeZrP_3O_{12}$ was prepared by sol-gel method and used as a mild and efficient solid acid catalyst for Friedel-Crafts benzylation of various arenes with benzyl bromide under solvent-free conditions. The method is green and has high yields.

Keywords: $K_2FeZrP_3O_{12}$, PIZP, Friedel-Crafts benzylation, solvent-free, sol-gel method, solid acid.

Introduction

Friedel–Crafts alkylation is one of most important and useful method for C-C bond formation in organic synthesis, which can be employing for producing fine chemicals such as cumene as intermediate for synthesis of phenol, long chain alkylbenzenes as intermediates for detergents. In these reactions generally stoichiometric amounts of acid catalyst such as mineral acid, anhydrous $AlCl_3$, etc. and solvents like nitrobenzene with high temperatures and large excess of arenes are used.[1-4]

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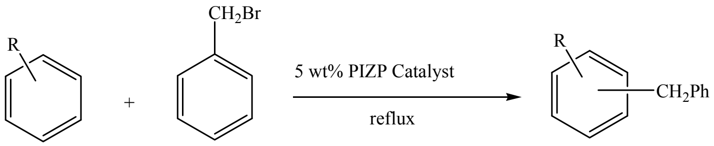
There is growing interest in replacing strong mineral acid, homogeneous, corrosive and polluting catalysts in producing of various fine chemicals with environmentally clean heterogeneous solid acid catalysts. Solid acids have many advantages such as straightforward handling, decreasing reactor and plant corrosion problem and environmentally safe disposal. Solid acid such as zeolite and clays,[5] sulfated zirconia,[6] nafion-silica,[7] alumina-supported niobia[8] and UDCaT-4[9] have been used for Friedel–Crafts alkylation. In continuation of our ongoing project for developing efficient solid acid,[10,11] we found that potassium iron zirconium phosphate (PIZP) can be used as an efficient and heterogeneous solid acid for Friedel-Crafts benzylation under mild conditions. PIZP catalyst was prepared by the reported sol-gel procedure that offers better control over surface, pore volume and pore size.[12-14] This catalyst has been used for Friedel–Crafts benzoylation.[15] This catalyst is stable and non-hygroscopic solid material and is insoluble in organic solvents.

Results and Discussion

Characterization of catalyst

In continuation of our efforts to develop facile and green chemistry,[16-18] in this paper we report the preparation of PIZP according to reported procedure and characterize it by comparing to authentic sample[15] and test the ability of this catalyst for benzylation of aromatic compounds under solvent-free conditions (Scheme 1) which results are summarized in Table 1. The catalyst can be kept under nitrogen atmosphere, in a desiccator on P_2O_5 and used for months without decreasing its activity, while by keeping the catalyst in laboratory after a week its activity decreased darmatically and this was not mentioned by others.[15] To optimize the reaction conditions, initially we studied the benzylation of anisole with benzyl bromide in the presence of 20 wt% PIZP in different solvent such as dichloromethane, acetonitrile and 1,2-dichloroethane under refluxing conditions, however the reaction did not complete after 5 hours. Therefore, the reaction was refluxed without using any solvent and the reaction was completed in 15 min with quantitative yields.



R= $-CH_3$, 1,2-$(CH_3)_2$, 1,3-$(CH_3)_2$, 1,4-$(CH_3)_2$, 1,3,5-$(CH_3)_3$, $-OCH_3$, -Cl, -Br

Scheme 1. Benzylation of aromatic compounds under solvent-free conditions

Table 1. Benzylation of various arenes with benzyl bromide using 5 wt% of PIZP under solvent-free conditions [a, b, c].

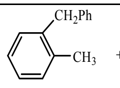
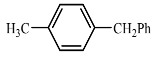
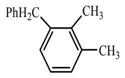
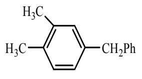
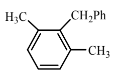
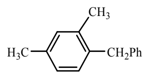
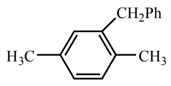
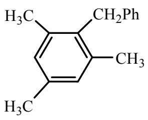
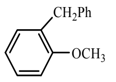
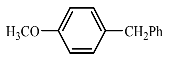
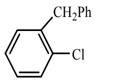
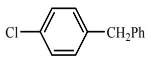
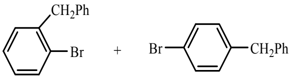
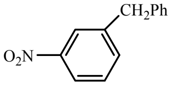
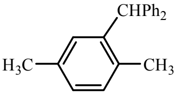
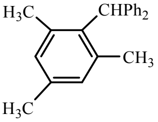
Entry	Substrate	R	Product		Time (min)	Conversion	Yield (%) (A/B)
			A	B			
1	Toluene	CH_3			15	100	82 (40:60)
2	o-Xylene	1,2-$(CH_3)_2$			10	100	80 (29:71)
3	m-Xylene	1,3-$(CH_3)_2$			10	100	75 (21:79)
4	p-Xylene	1,4-$(CH_3)_2$			15	100	75
5	Mesitylene	1,3,5-$(CH_3)_3$			10	100	80
6	Anisol	OCH_3			15	100	78 (40:60)
7	Chlorobenzene	Cl			45	100	76 (14:86)

Table 1. Continued

8	Bromobenzene	Br		50	100	73 (14:86)
9	Nitrobenzene	NO_2		300	0	0
10	p-Xylene[d]	1,4-$(CH_3)_2$		180	70	52
11	Mesitylene[d]	1,3,5-$(CH_3)_3$		180	0	0

[a] The yields refer to the isolated pure products.
[b] The products were characterized from their spectral (IR, ^{1}H NMR).
[c] The ratio of A and B products were determined by ^{1}H NMR.
[d] Bromodiphenyl methane was used as alkylating agent.

Optimization the amount of catalyst

To optimize the amount of catalyst, we did the reaction of anisole with benzyl bromide in the presence of different amounts of catalyst (Table 2). As shown in Table 2, when large amount (10 and 20 wt%) of PIZP is used the reaction time is increased because PIZP catalyst by Zr^{4+} and Fe^{3+} ions that are strong Lewis acid can interact with the anisole moreover benzyl bromide and decrease the nucleophilicity of the anisole. Based on the yield and reaction time, the 5 wt% PIZP was the best amount of catalyst. Therefore, we employed 5 wt% PIZP for conversion of various aromatic compounds (Table 1).

Table 2. Optimization of amount of PIZP for 100 % benzylation of anisole under solvent-free conditions.

Time (min)	95	30	15	15	20	120
Wt% Catalyst	2	3	4	5	10	20

Efficiency of catalyst

In comparison with reported solid acids this catalyst obtained through the reported method showed priority due to the using molar ratio of the catalyst, reaction rate and the yield of product (Table 3). The catalytic nature of potassium iron zirconium phosphate can be attributed to the presence of Zr^{4+} and Fe^{3+} captions which act as strong Lewis acid. In this method the work-up was straightforward and the catalyst was simply filtered off from the reaction mixture. By using this catalyst, various aromatic compounds were converted to their corresponding alkyl benzenes in good yields and short time. This method can be employed for benzylation of various arenes including electron-releasing substituent (Table 1, entries 1-6) and electron withdrawing substituent (Table 1, entries 7-8), however the reaction time for the latter is longer. The reaction of nitrobenzene with benzyl bromide was done for 5 hours but the product was not observed (Table 1, entry 9). Additionally, bromodiphenylmethane as a hindered alkylating agent was employed in this reaction. The reaction of p-xylene with bromodiphenylmethane was done for 3 hours but the yield of product was moderate to low (Table 1, entry 10). About mesitylene (as a hindered substrate) with the same hindered alkylating agent, no product was observed after 3 hours (Table 1, entry 11). Furthermore, we examined the reaction of p-xylene with other alkylating agents such as 2-nitrobenzyl chloride and benzyl alcohol in the presence of PIZP but the product was not detected.

Table 3. Catalytic activity of PIZP for benzylation of toluene in comparison with reported methods.

Catalyst [Ref.]	Mol% (Wt%)	Solvent	Arene (mmol)	Time	Temprature (K)	Yield (%)
PIZP	(5)	none	Toluene (5)	15 min	reflux	82
Nb_2O_5/Al_2O_3 [8]	(78)	none	Anisol (150)	100 mir	433	78
$InCl_3$ [19]	10	CH_2Cl_2	p-xylene (5)	16 h	298	100
$Cl_2Si(OTf)_2$ [20]	10	none	Toluene (10)	4.5 h	323	50
$Sc(OTf)_3$ [21]	10	none	Anisol (5)	1 h	388	87
HAP [22]	(88)	none	Toluene (94)	2 h	reflux	93

Experimental

General

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by spectroscopy data (IR, ^1H NMR spectra). ^1H-NMR spectra were recorded at FT-300 MHz. The spectra were measured in $CDCl_3$ relative to TMS (0.00 ppm).

Catalyst preparation

PIZP was synthesized according to reported procedure and characterized by FT-IR comparing with authentic sample.[15] FT-IR (KBr): 1100, 1045, 1020, 990, 640, 595, 555, 450, 1100, 1070, 1009, 870, 576. The catalyst can be kept unedr nitrogen atmosphere, in a desiccator on P_2O_5 and used for months without decreasing its activity.

Catalyst activity

In a 25 ml round bottomed flask equipped with a reflux condenser, magnetic stirrer and $CaCl_2$ guard tube, a mixture of 5 mmol of aromatic compounds, 1 mmol of benzyl bromide and catalyst (5 wt% related to benzyl bromide) was refluxed for the time specified in Table 1. The reaction was followed by TLC (eluent, cyclohexane). After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was filtered off and the solid was washed with CH_2Cl_2 (10 ml). The organic layer was washed with 10% $NaHCO_3$ (3×5 ml) and water (10 ml) and the organic phase was dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under reduced pressure to give the pure desired compound and characterized by ^1H-NMR and FT-IR.

1-Benzyl-4-methylbenzene and 1-benzyl-2-methylbenzene: ^{1}H-NMR δ: 7.1–7.5 (m, 9 H), 4.15 (s, 0.66H), 4.05 (s, 1.34H), 2.45 (s, 1.81H), 2.35 (s, 1.19H) ppm.

2-benzyl-1,4-dimethylbenzene: ^{1}H-NMR δ: 6.8-7.2 (m, 8H), 3.9 (s, 2H) 2.2 (s, 3H), 2.15 (s, 3H) ppm.

2-benzyl-1,3,5-trimethylbenzene: ^{1}H-NMR δ: 6.9-7.25 (m, 7H), 4.05 (s, 2H) 2.3 (s, 3.04H), 2.22 (s, 5.96H) ppm.

1-benzyl-4-methoxy benzene and 1-benzyl-2-methoxybenzene: ^{1}H-NMR δ: 6.9–7.35 (m, 9H), 4.1 (s, 1.27H), 4.03 (s, 1.73H), 3.9 (s, 0.81H), 3.86 (s. 1.19H) ppm.

1-benzyl-2,4-dimethylbenzene and 2-benzyl-1,3-dimethylbenzene: ^{1}H-NMR δ: 7.95–7.25 (m, 8H), 4.08 (s, 0.42H), 3.95 (s. 1.58H), 2.3 (s, 2.83H), 2.25 (s, 1.13H) 2.2 (s, 2.04H) ppm.

4-benzyl-1,2-dimethylbenzene and 1-benzyl-2,3-dimethylbenzene: ^{1}H-NMR δ: 6.8-7.2 (m, 8H), 3.95 (s, 0.57H), 3.85 (s, 1.43H), 2.22 (s, 1.08H), 2.15 (s, 3.84H) 2.05 (s, 1.08H) ppm.

1-benzyl-4-chlorobenzene and 1-benzyl-2-chlorobenzene: ^{1}H-NMR δ: 6.9-7.3 (m, 9H), 4.05 (s, 0.29H), 3.85 (s, 1.71H) ppm.

1-benzyl-4-bromobenzene and 1-benzyl-2-bromobenzene: ^{1}H-NMR δ: 6.9-7.4 (m, 9H), 4.05 (s, 0.29H), 3.85 (s, 1.71H) ppm.

Catalyst reusability

The catalyst was recoverd by filtration off and washing with acetone and ether. The reusability of the catalyst was checked by testing the reaction by using the same batch the catalyst system. After each reaction the catalyst was filtered off, washed with acetone and ether and dried, then reused for another reaction. After reusing the catalyst for 5 times, the activity was reduced by 5-6 %.

Conclusions

In conclusion, we have developed a facile, convenient and solvent-free method for the synthesis of alkyl benzenes from aromatic compounds and benzyl bromide using catalytic amount of PIZP as an efficient catalyst. The use of non-toxic and easy prepared and recyclable catalyst is other advantages of this method. Further investigation on the new application of PIZP is ongoing in our groups.

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