

# A novel sol–gel synthesized catalyst for Friedel–Crafts benzoylation reaction under solvent-free conditions

M.B. Gawande, S.S. Deshpande, S.U. Sonavane, R.V. Jayaram\*

*Applied Chemistry Division, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400019, India*

Received 31 March 2005; received in revised form 27 May 2005; accepted 24 June 2005

Available online 19 August 2005

## Abstract

The catalyst potassium iron zirconium phosphate [PIZP] was prepared by sol–gel method. The as-synthesized material was characterized by crystal size, elemental analysis, BET surface area, pore volume, average pore diameter, XRD, FTIR and DSC techniques. The catalytic activity was tested for the benzoylation of different arenes using benzoyl chloride as benzoylating agent. The reaction was carried out at different temperatures and catalyst loadings.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* PIZP; Sol–gel method; Solvent-free; Friedel–Crafts benzoylation reaction

## 1. Introduction

Acylation of aromatics is a key reaction in organic chemistry. The resulting diaryl ketones are used in the production of various pharmaceutical products, agro chemicals and perfumery chemicals [1,2]. The replacement of homogeneous catalysts by solid acids for the Friedel–Crafts acylation is a challenging task. Numerous papers report attempts to turn the existing stoichiometric methods into catalytic process [3–6].

Friedel–Crafts acylation has been studied extensively over the past few decades using molar amounts of Lewis acids, such as  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{FeCl}_3$  and zeolites as catalysts. The major drawback of these catalysts is that they are non-recoverable. Other reported protocols involve the use of iron(III) sulphate [7], methanesulfonic acid [8], palladium [9], trimethylpolyphosphate [10], nafion-H [11], bismuth(III) trifluoromethane sulphonate [12], trifluoromethanesulphonic acid [13], bismuth(III) chloride and triflate [14],  $\text{Al}_2\text{O}_3\text{–ZrO}_2/\text{S}_2\text{O}_8^{2-}$  [15]. Despite substantial improvements, significant limitation still exists with respect to acylation reaction.

We have previously studied the activity of various metal oxide catalysts for several reduction and alkylation reactions [16–21]. The present investigation is a part of our ongoing programme on the catalytic efficiency of metal oxides. We, herein, report the application of potassium iron zirconium phosphate [PIZP] for the synthesis of diaryl ketones by Friedel–Crafts reaction of different arenes. The advantage of PIZP is that it can be prepared easily and does not lose its activity even after several runs.

## 2. Experimental

### 2.1. Preparation of catalyst

All chemicals of analytical grade (Aldrich) were used for catalyst preparation. The catalyst PIZP was prepared by the reported sol–gel procedure [22]. Sol–gel method have several advantages over other common methods such as precipitation, impregnation, etc. In general, sol–gel synthesis offers better control over surface, pore volume and pore size [23,24]. In a typical procedure, 6 mL of 1 M  $\text{H}_3\text{PO}_4$  was slowly added with constant stirring to an aqueous solution containing stoichiometric quantities of KCl (2 M),  $\text{FeCl}_3$  (1 M) and  $\text{ZrOCl}_2$

\* Corresponding author. Tel.: +91 22 24145616; fax: +91 22 24145614.  
E-mail address: [rvjayaram@udct.org](mailto:rvjayaram@udct.org) (R.V. Jayaram).

Table 1  
Elemental analysis (wt%) of K, Fe, Zr and P

Element	Elemental analysis	
	Calculated (%)	Experimental (%)
K	15.30	15.6
Fe	10.90	11
Zr	17.80	17.6
P	18.2	18.14

(1 M). The resultant gel was dried at 85 °C for 25 h, thoroughly dispersed in an agate mortar and then calcined at 600 °C for 8 h.

## 2.2. Catalyst characterization

The X-ray powder diffraction pattern was obtained using a conventional powder diffractometer (Philips 1050) using graphite monochromatized Cu K $\alpha$  radiation operating in Bragg-Brentano ( $\theta/2\theta$ ) geometry. Surface area measurement and pore size distribution analysis were done, after degassing the sample under high vacuum at 300 °C for 4 h, by nitrogen adsorption on a micromeritics ASAP 2010 instrument at an adsorption temperature of 77 K. The elemental analysis of K, Fe and Zr was done by Neutron activation analysis at a thermal neutron flux of  $1.3 \times 10^{12}$  n cm $^{-2}$  s $^{-1}$  in APSARA reactor and P content was determined using a ICP-AES spectrometer. Both these measurements were carried out at BARC, Mumbai. The Fourier transform infrared spectrum (FTIR) of the sample was recorded on a Nicolet-360 FTIR spectrometer using KBR pellet. The DSC measurements were carried out with a Perkin-Elmer differential scanning calorimeter (pyris 6 DSC).

## 2.3. Analytical procedure

See Table 1.

## 2.4. X-ray diffraction studies

From the XRD, percentage crystallinity of catalyst was found out. It was near about 65% and crystallite size of the catalyst is 1.65 nm, calculated by using Scherrer's equations after correcting the line width at half maxima for instrumental line broadening (Fig. 1).

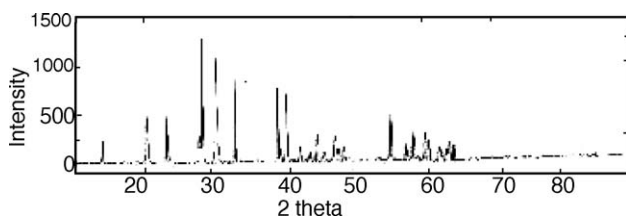


Fig. 1. X-ray powder diffraction pattern of PIZP.

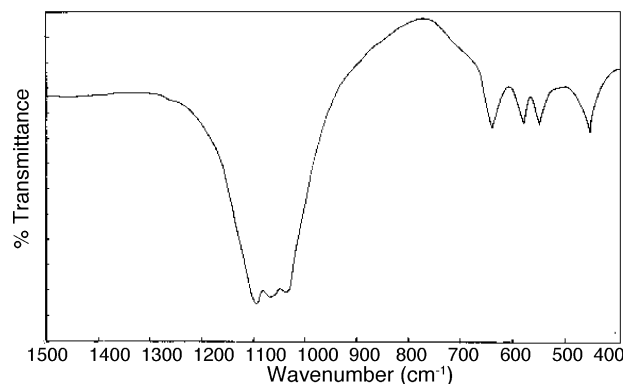


Fig. 2. IR spectrum of PIZP.

## 2.5. FTIR measurements

IR studies were carried out to ascertain the M–O interactions and the IR active stretching vibrations and  $\nu_2 = 2F$  and  $\nu_4 = 3F$  for the bending vibrations. The bands in the range 1100–990 cm $^{-1}$  are due to the P–O stretching frequencies in the PO $_4$  tetrahedron:  $\nu_3$  1100, 1045 and 1020 cm $^{-1}$ ;  $\nu_1$  shoulder 990 cm $^{-1}$ . The 640–550 region shows three bands expected for  $\nu_4$  bending vibrations: 640, 595 and 555 cm $^{-1}$ . The 450 cm $^{-1}$  peak could be contributed to  $\nu_2$ . The spectral observations are in line with the reported results [23] (Fig. 2).

## 2.6. DSC of PIZP

Definite amount (0.7 mg) of the sample was taken and the temperature was raised from 36 to 400 °C at a heating rate 10 °C/min.

Absence of an endotherm between 90 and 260 °C in the DSC of samples calcined at 500, 400 and 300 °C indicates that there is no loss of physisorbed water. However, the sample calcined at 600 °C shows an endotherm between 90 and 260 °C (Fig. 3) which may be due to the removal of physisorbed water. It is well known that calcinations result in a gradual removal of water that converts Brønsted acidic centers to Lewis acidic centers [25,26]. At about 280 °C, the removal of physisorbed water is complete. There is also an endotherm between 280 and 400 °C which possibly indicates commencement of further formation of Lewis acid sites on the surface (Fig. 4).

## 2.7. BET surface area and pore size analysis

The textural characterization of PIZP was performed by BET surface area, pore volume and average pore diameter measurements (Table 2).

## 2.8. Catalytic activity

The reactions were carried out in a 25 mL round bottom flask equipped with a reflux condenser, magnetic stirrer and

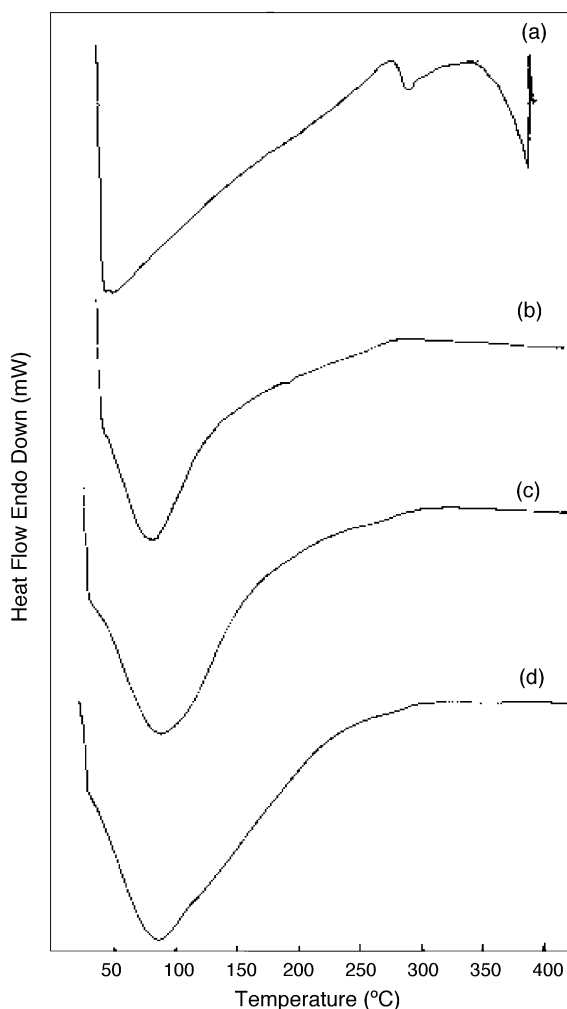


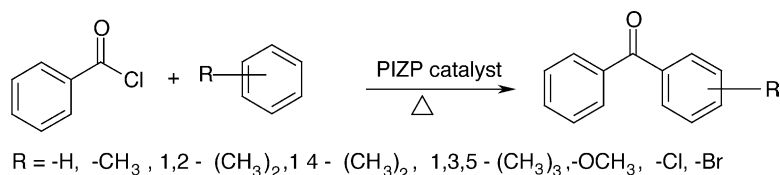
Fig. 3. Calcined at: (a) 600 °C; (b) 500 °C; (c) 400 °C; (d) 300 °C.

Table 2

BET surface area and pore size analysis of PIZP

Catalyst	PIZP
BET surface area (m <sup>2</sup> /g)	29.4
Pore volume (cm <sup>3</sup> /g)	0.054
Average pore diameter (Å)	73.84

CaCl<sub>2</sub> guard tube. The 0.1 mole of substrate, 0.02 mole of benzoyl chloride and catalyst (20 wt%) were added and the flask heated in a thermostated oil bath at the required temperature. The HCl evolved during the reaction was absorbed in an alkali solution. The reaction products were analyzed by TLC. After completion of the reaction, the reaction mixture was



Scheme 1. Friedel–Crafts benzylation of arenes with benzoyl chloride.

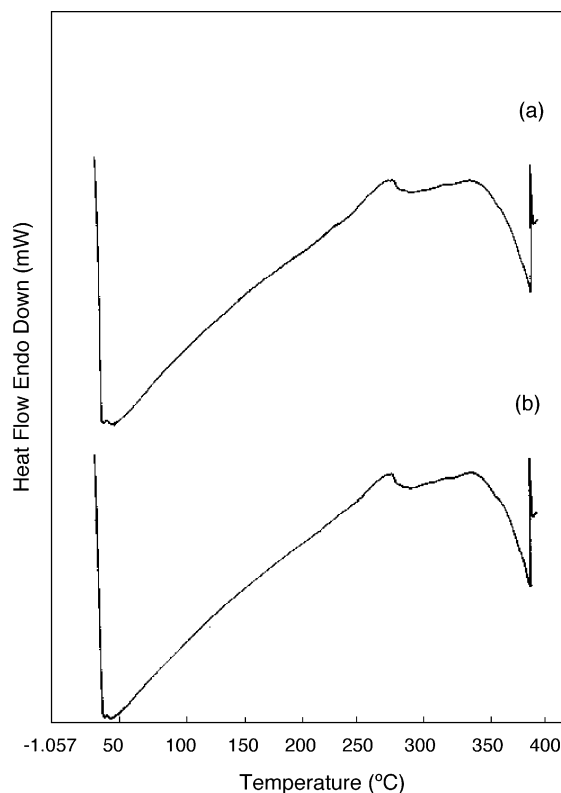


Fig. 4. DSC for: (a) fresh PIZP and (b) spent PIZP.

cooled to room temperature and the catalyst was filtered off and the catalyst washed with acetone. In the obtained liquid, Et<sub>2</sub>O (10 mL) was added; the organics was washed with 5% NaHCO<sub>3</sub> (15 mL) successively and then dried with MgSO<sub>4</sub>. Evaporation of the solvent under reduced pressure afforded the crude product. The crude product was purified by recrystallization with ethanol or column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent to afford pure product. Percentage of *ortho*, *meta*, and *para* isomers were determined by using gas chromatograph fitted with OV-17 (Eshita, Model-Eshika).

### 3. Results and discussion

#### 3.1. Benzylation of substituted arenes over PIZP

Eight substituted arenes were investigated at various temperatures, as specified, in a batch reactor (Scheme 1). Most of the earlier work on benzylation of arenes has been carried

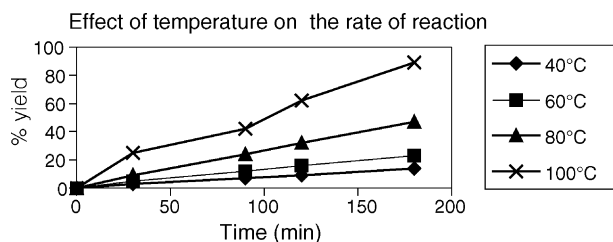


Fig. 5. Effect of temperature on the benzoylation of 1,2-dimethyl benzene by benzoyl chloride. *Reaction conditions:* time 2.5 h, solvent-free, 1,2-dimethyl benzene = 0.1 mol, benzoyl chloride = 0.02 mol, catalyst amount 20 wt%.

Table 3

Effect of catalyst loading on the benzoylation of 1,2-dimethyl benzene with benzoyl chloride

Sr. no.	Catalyst (wt%)	Yield (%)
1	5	23
2	10	42
3	15	60
4	20	89

*Conditions:* 1,2-dimethyl benzene = 0.1 mol, benzoyl chloride = 0.02 mol; catalyst amount = 20 wt%; time 2.5 h, solvent-free.

at 100 °C. However, in the present case, the yield was better than those reported [15].

In Hammett equation, sigma ( $\sigma$ ) value is the substituent constant. It is known that positive sigma ( $\sigma$ ) value indicates the electron withdrawing effect of substituent attached to the aromatic nucleus and negative sigma ( $\sigma$ ) value indicates electrons releasing effect. The predominance of one isomer (*para*) over the other (*meta*) is explained on the basis of sigma ( $\sigma$ ) value of the substituents (Table 4). As the  $\sigma_p$  (negative sigma value for *para* isomer) for CH<sub>3</sub> group (entry 2, Table 4) is greater than  $\sigma_m$  (negative sigma value for *meta* isomer), the major formation of *para* is justified. Similar analogy is applicable to electron withdrawing substituents (entries 5 and 7, Table 4) as well.

### 3.2. Effect of temperature

Reactions were carried out at various temperatures (Fig. 5). The maximum conversion were 14% at 40 °C, 23% at 60 °C, 47% at 80 °C and 89% at 100 °C. There was substantial increase in the conversion between 40 and 100 °C.

Table 4

Benzoylation of different arenes with benzoyl chloride using PIZP catalyst

Entry	Substrate	Temperature (°C)	Time (h)	$\sigma_p/\sigma_m$	Yield (%) ( <i>o</i> -/ <i>l</i> -/ <i>m</i> -/ <i>p</i> )
1	Benzene	80	3.5	–	87
2	Toluene	100	3	(–0.17/–0.06)	90 (17:3:80)
3	<i>O</i> -xylene	100	2.5	–	89
4	<i>p</i> -Xylene	100	2.5	–	93
5	Chlorobenzene	135	3	(0.22/0.37)	87 (11:1:88)
6	Anisole	100	1	(–0.29/0.11)	94
7	Bromobenzene	150	3	(0.23/0.40)	88 (9:1:90)
8	Mesitylene	110	2.5	–	96

*Conditions:* substrate = 0.1 mol; benzoyl chloride = 0.02 mol; PIZP (catalyst) = 20 wt%, solvent-free. Isolated yield, the products were characterized by IR and NMR techniques. Anisole gave exclusively *para* isomer.

Table 5

Reyclability of PIZP in the benzoylation of 1,2-dimethyl benzene with benzoyl chloride

Sr. no.	Cycle	Yield (%)
1	0	89
2	1	88
3	2	85
4	3	87
5	4	86
6	5	85

*Conditions:* 1,2-dimethyl benzene = 0.1 mol; benzoyl chloride = 0.02 mol, catalyst amount = 20 wt%; time 2.5 h, solvent-free.

### 3.3. Effect of catalyst loadings

See Tables 3 and 4.

### 3.4. Reusability of PIZP

Reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst system. After each cycle, the catalyst was filtered off, washed with acetone and ether successively, dried and then used for successive cycles. It was observed that the activity of PIZP slightly decreased on subsequent runs. After five cycles, the activity was reduced by just about 3–4%.

In order to check the reusability of the catalyst, we carried out benzoylation of 1,2-dimethyl benzene with benzoyl chloride under solvent-free conditions. The results are depicted as below (Table 5).

In addition to this, the DSC of spent catalyst Fig. 4(b) was compared with that of the fresh one Fig. 4(a). The comparison indicated that there is no change in the endothermic peak, which indicate that the catalyst remains active for the second cycle.

### 3.5. Effect of PIZP over reaction

The catalytic activity of the system is mainly due to interaction between Zr and Fe atoms. Since the electronegativity of Fe<sup>3+</sup> (1.83 eV) is higher than that of Zr<sup>4+</sup> (1.33 eV), the partial charge on Zr is increased in PIZP. This is in consonance with the fact that in case of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2–</sup>, there is an increase in the zirconium partial charge [15,27,28].

This may help to stabilize the surface of the catalyst and to increase the number of strong acid sites for the acylation reaction. Another important observation is that the catalyst calcined at 600 °C was of higher activity compared to catalysts calcined at lower temperatures. It may be due to the conversion of Brønsted acidic sites into Lewis acidic sites at higher calcination temperature.

#### 4. Conclusion

PIZP, a solid acid catalyst prepared by sol–gel method, was found to be an efficient candidate for the benzylation of arenes with benzoyl chloride under solvent-free conditions. The activity of the catalyst was almost constant after five cycles. DSC of fresh and spent catalyst indicated that the active sites remain intact. It was also found that the catalyst calcined at 600 °C was of maximum activity.

#### Acknowledgements

This work is dedicated to late Dr. A.K. Vanjara. The authors are thankful to Prof. Akamanchi for providing the DSC facility and MBG is grateful to Sandip Maind for elemental analysis, to TIFR for providing XRD and also thanks to Prof. S.D. Samant for his kind support.

#### References

- [1] A. Cornelis, P. Laszlo, S. Wang, *Tetrahedron Lett.* 34 (1993) 3849.
- [2] F. Effenberger, J.K. Eberhard, A.H. Maier, *J. Am. Chem. Soc.* 118 (1996) 12572.
- [3] F. Effenberger, G. Epple, *Angew. Chem. Int. Ed.* 84 (1972) 295.
- [4] F. Effenberger, E. Sohn, G. Epple, *Chem. Ber.* 116 (1983) 1195.
- [5] I. Hachija, M. Moriwaki, S. Kobayashi, *Bull. Chem. Soc. Jpn.* 68 (1995) 2053.
- [6] I. Hachija, M. Moriwaki, S. Kobayashi, *Tetrahedron Lett.* 36 (1995) 409.
- [7] J.O. Morley, *Synthesis* (1977) 54.
- [8] V. Premasgar, V.A. Palaniswamy, E.J. Eisenbraun, *J. Org. Chem.* 46 (1981) 2974.
- [9] T. Ishiyama, K. Kizaki, N. Miyarura, A.S. Suzuki, *Tetrahedron Lett.* 34 (1993) 7595.
- [10] E.M. Bermon, H.D. Showwalter, *J. Org. Chem.* 54 (1989) 5642.
- [11] T. Yamato, C. Hedishima, G.K. Surya Prakash, G.A. Olah, *J. Org. Chem.* 56 (1991) 3955.
- [12] S. Repichet, C. Le Roux, J. Dubac, J.R. Desmurs, *Eur. J. Org. Chem.* (1998) 2743.
- [13] J.P. Hwang, G.K. Surya Prakash, G.A. Olah, *Tetrahedron* 56 (2000) 7199.
- [14] C. Le Roux, J. Dubac, *Synlett* 2 (2002) 181.
- [15] T.S. Jin, M.N. Yang, G.L. Feng, T.S. Li, *Synth. Commun.* 34 (2004) 479.
- [16] S.U. Sonavane, R.V. Jayaram, *Synth. Commun.* 33 (2003) 843.
- [17] S.U. Sonavane, R.V. Jayaram, *Synlett* 1 (2004) 146.
- [18] P. Selvam, S.U. Sonvane, R.V. Jayaram, *Adv. Synth. Catal.* 346 (2004) 542.
- [19] S.K. Mohapatra, S.U. Sonvane, R.V. Jayaram, P. Selvam, *Org. Lett.* 24 (2002) 4297.
- [20] A.S. Kulkarni, R.V. Jayaram, *Appl. Catal.* 252 (2003) 225.
- [21] S.N. Koyande, R.G. Jaiswal, R.V. Jayaram, *Ind. Eng. Chem. Res.* 37 (1998) 908.
- [22] A.I. Orlova, I.G. Trubach, V.S. Kurazhkovskaya, P. Petrierra, M.A. Salgado, S. Garcia-Granda, S.A. Khanakov, J.R. Garcia, *J. Solid State Chem.* 173 (2003) 314.
- [23] C. Perego, P. Villa, *Catal. Today* 34 (1997) 281.
- [24] R.D. Gonzalez, T. Lopez, R. Gomez, *Catal. Today* 35 (1997) 293.
- [25] S.G. Pai, A.R. Bajpai, A.B. Deshpande, S.D. Samant, *J. Mol. Catal.* 156 (2000) 233.
- [26] C. Catieviela, F. Figuras, J.M. Fraile, J.I. Gracia, J.A. Mayaoral, L.C. de Menorval, E. Pires, *Appl. Catal. A Gen.* 101 (1993) 253.
- [27] B. Duricic, S. Pickering, P. Glaude, D. Mcgravrry, P. Tambuysen, *J. Mater. Sci.* 32 (1997) 589.
- [28] S. Damyanova, P. Grange, B. Delmon, *J. Catal.* 168 (1997) 421.