

PbO as an efficient and reusable catalyst for one-pot synthesis of tetrahydro benzo pyrans and benzylidene malonitriles

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MS received 18 January 2012; revised 11 October 2012; accepted 17 October 2012

Abstract. PbO nanoparticles have been employed as an efficient catalyst for the solvent-free synthesis of tetrahydrobenzo pyrans (yields 81–91%) and benzylidene malonitriles (yields 90–96%) at room temperature using green chemistry approach. PbO nanoparticles were found to be highly efficient, eco-friendly and recyclable heterogeneous catalyst. PbO nanoparticles were prepared by hydrothermal method and characterized by IR, XRD, BET Surface area, SEM, EDAX and TEM with SAED techniques.

Keywords. PbO nanoparticles; tetrahydrobenzo pyrans; benzylidene malonitriles; grinding; solvent-free.

1. Introduction

Benzopyrans and their derivatives are known to show several pharmacological properties such as spasmolytic, diuretic, antianaphylactin, antisterility and are used as anticancer agents.¹ The polyfunctionalized benzopyrans are also used as cosmetics, pigments and biodegradable agrochemicals.² The benzylidene malonitrile derivatives have been found to possess inhibitory activity to HER2,³ EGFR,⁴ IGF1R⁵ and have been used for treatment of cancer.⁶ Many synthetic procedures have been reported for tetrahydro benzo pyrans and benzylidene malonitriles.

The tetrahydro benzo pyrans have been previously synthesized by two or three-component condensations including the use of catalysts like potassium phosphate,⁷ ZnO-beta zeolite,⁸ Ce(SO₄)₂·4H₂O,⁹ s-proline,¹⁰ caro's acid-silica gel,¹¹ hexadecyl trimethyl ammonium bromide,¹² sulphonic acid functionalized silica,¹³ tetra butyl ammonium bromide,¹⁴ rare earth perfluorooctanoate,¹⁵ basic quaternary ammonium salt,¹⁶ phenyl boronic acid,¹⁷ LiBr,¹⁸ TEAA,¹⁹ PEG-400,²⁰ basic ionic liquid,²¹ amines²² and (NH₄)₂HPO₄.²³ The benzylidene malonitriles were synthesized using catalysts such as calcium oxide,²⁴ TEBA,²⁵ PEG,²⁶ base,²⁷ NH₂SO₃NH₄,²⁸ MgBr₂·OEt₂,²⁹ organo-base mediation,³⁰ quaternary ammonium salts,³¹ Na₂S/Al₂O₃,³² mpg-C₃N₄,³³ mesoporous base,³⁴ zirconia,³⁵ amine supported on silica gel³⁶ and MgC₂O₄/SiO₂.³⁷

Recently, metal oxide nanoparticles in the form of nanocatalyst have emerged as viable alternatives to conventional materials in various fields of chemistry and attracted marvelous interest of chemists. Metal oxide nanoparticles are known to be promising heterogeneous catalysts in a variety of organic transformations.³⁸ Nanoparticles have the potential for improving the efficiency, selectivity and yield of catalytic processes. In particular, the PbO nanoparticles provide higher surface to volume ratio in the reaction. Higher selectivity of PbO nanoparticles towards reaction proceeds through less waste and fewer impurities, which could lead to safer technique and reduced environmental impact. PbO nanoparticles have been investigated as catalysts in the organic reactions including the Paal-Knorr reaction and oxidative coupling of methane.^{39,40} Thus, the significant catalytic property with operational simplicity, high reactivity, environmental friendliness, reduced reaction times and reusability of PbO nanoparticles have prompted us to employ as catalyst for multicomponent reaction.

In view of the importance of PbO nanoparticles as a catalyst in organic synthesis, we report here a simple solvent-free synthesis of tetrahydrobenzo pyrans and benzylidene malonitriles. In this study, PbO nanoparticles were synthesized by hydrothermal method and characterized by IR, XRD, BET Surface area, SEM, EDAX and TEM with SAED techniques. In view of emerging importance of heterogeneous catalyst, we wish to explore the applications of PbO nanoparticles as a catalyst in organic synthesis.

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2. Experimental

The synthesized PbO nanoparticles were characterized by FTIR using Shimadzu 8400 s instrument. XRD pattern was recorded using Phillips-1710 diffractometer with Cu- α radiation ($\lambda = 1.54 \text{ \AA}$). The surface area was recorded with the help of Quantachrome Autosorb Automated Gas Sorption System. SEM and EDAX were recorded using JEOL-JEM-6360 microscope. TEM was recorded with SAED using CM-200 Philips Microscope. Melting points were determined using open capillary tubes on Veego melting point apparatus and are uncorrected. FTIR spectra were recorded on Shimadzu 8400 s spectrometer using KBr pellets. ^1H NMR spectra were recorded on a Bruker Advance II 400 MHz spectrometer in DMSO- d_6 with TMS as an internal standard.

2.1 Synthesis of PbO nanoparticles

A mixture of citric acid (2.5 mmol) and sodium hydroxide (10 ml, 0.1 N) in distilled water was added to a magnetically stirred methanolic solution of lead nitrate (2 mmol). The reaction mixture was stirred for 2 h at room temperature. The white polycrystalline product

was filtered, washed with distilled water and dried at 110°C for 2 h. The solid product was calcinized at 500°C for 2 h. Over the course of this process, the white PbO nanoparticles turned pale yellow colour.

2.2 Synthesis of tetrahydro benzo pyran derivatives

A mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol), dimedone (1 mmol) and PbO nanoparticles (50 mg) were ground at a room temperature with a mortar and pestle. The reaction was monitored by thin-layer chromatography (TLC). After completion of reaction, the product was washed with distilled water. The crude product was dried and recrystallized from ethanol to afford pure compounds with high yield (table 1; scheme 1).

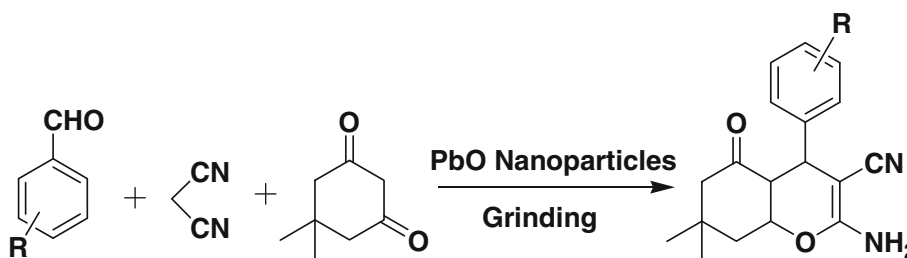
2.3 Spectroscopic data

2.3a *Compound (table 1, 4a)*: IR (KBr, cm^{-1}): 3392, 3319, 3182, 2954, 2192, 1681, 1656, 1360 cm^{-1} ^1H NMR (400 MHz, DMSO- d_6): 0.94 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.08 (d, $J = 16.0 \text{ Hz}$, 1H), 2.23 (d, $J = 16.0 \text{ Hz}$, 1H), 2.50 (m, 2H, CH_2), 4.11 (s, 1H), 7.06 (s,

Table 1. PbO nanoparticles catalysed synthesis of tetrahydro benzo pyrans.

Entry	Product (R group)	Time (min)	Yield (%)	M. P. ($^\circ\text{C}$) observed (reported) ^{ref.}
4a	H	15	83	229 (227–229) ¹⁴
4b	4-Cl	12	90	212 (212–214) ¹⁴
4c	4-OMe	18	85	201 (201–203) ¹⁴
4d	2-Cl	15	86	202 (200–202) ¹²
4e	4-NO ₂	10	91	180 (178–180) ¹⁴
4f	4-OH	15	82	208 (206–208) ¹⁰
4g	3-NO ₂	15	85	212 (210–212) ¹⁴
4h	3-OH	15	81	236 (236–238) ¹⁰
4i	2-Furyl	20	85	198 (196–198) ²¹
4j	2-Thienyl	20	83	211 (210–212) ²¹

All the products are known compounds and were identified by comparison of their melting points and spectral data those with reported^{10,12–14,21}



Scheme 1. Synthesis of tetrahydro benzo pyrans.

Table 2. PbO nanoparticles catalysed synthesis of benzylidene malonitriles.

Entry	Product (R group)	Time (min)	Yield (%)	M. P. (°C) observed (reported) ^{ref.}
3a	H	09	91	88 (87–88) ²⁸
3b	4-OMe	13	92	115 (115–116) ²⁶
3c	3-NO ₂	19	95	102 (102–103) ²⁶
3d	4-OH	25	93	185 (185–186) ²⁶
3e	4-NO ₂	09	96	160 (159–160) ²⁶
3f	2-Cl	26	90	94 (94–96) ²⁶
3g	4-Cl	13	92	162 (162–163) ²⁸
3h	2-NO ₂	18	90	139 (138–139) ²⁵

All the products are known compounds and were identified by comparison of their melting points and spectral data with those reported^{25,26,28}

br, 2H, NH₂), 7.19 (m, 3H, ArH), 7.33 (m, 2H). MS (m/z) = 294 (M + 1).

2.3b Compound (table 1, 4b): IR (KBr, cm⁻¹): 3303, 3041, 2994, 2246, 1653, 1613, 1490, 850 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): 1.07 (s, 3H, CH₃), 1.12 (s, 3H, CH₃), 2.26 (s, 2H, CH₂), 2.46–2.48 (m, 2H, CH₂), 4.43 (s, 1H, CH), 6.58 (s, 2H, NH₂), 7.18–7.28 (m, 4H, ArH). MS (m/z) = 328 (M + 1).

2.3c Compound (table 1, 4c): IR (KBr, cm⁻¹): 3400, 3300, 3040, 2990, 2240, 1680, 1510, 840 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): 1.03 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.21 (d, J = 16.0 Hz, 1H), 2.22 (d, J = 16.0 Hz, 1H), 2.43 (s, 2H), 3.77 (s, 3H), 4.36 (s, 3H), 4.55 (s, 2H), 6.84 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H). MS (m/z) = 324 (M + 1).

2.3d Compound (table 1, 4e): IR (KBr, cm⁻¹): 3394, 3323, 3213, 2970, 2193, 1683, 1523, 1365 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): 0.99 (s, 3H, CH₃), 1.06 (s, 3H, CH₃), 2.14 (d, J = 16.0 Hz, 1H), 2.30 (d, J = 16.0 Hz, 1H), 2.53–2.57 (m, 2H, CH₂), 4.39 (s, 1H), 7.24 (s, 2H, NH₂), 7.48 (d, 2H, J = 8.4 Hz, ArH), 8.21 (s, J = 8.4 Hz, 2H, ArH). MS (m/z) = 339 (M + 1).

2.4 Synthesis of benzylidene malonitrile derivatives (scheme 2)

A mixture of aromatic aldehydes (1 mmol), malonitrile (1 mmol) and PbO nanoparticles (40 mg) was ground in the presence of sunlight at room temperature. The reaction was monitored by TLC. After completion of reaction, the crude product was washed with distilled water, dried and recrystallized from alcohol to afford pure product (table 2).

2.5 Spectroscopic data

2.5a Compound (table 2, 3c): IR (KBr, cm⁻¹): 3107, 2225, 1945, 1610, 1595, 1529, 1479 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): 7.86 (s, 1H), 8.31 (s, 1H, = CH), 8.33–8.45 (m, 3H). MS (m/z) = 200 (M + 1).

2.5b Compound (table 2, 3d): IR (KBr, cm⁻¹): 3350, 3026, 2223, 1569, 1511 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): 6.91 (d, J = 6.4 Hz, 2H, ArH), 7.89 (s, 2H, ArH), 7.97 (s, 1H, = CH). MS (m/z) = 171 (M + 1).

2.5c Compound (table 2, 3e): IR (KBr, cm⁻¹): 2231, 1607 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): 8.12 (d, 2H, J = 8.8 Hz, ArH), 8.31 (d, J = 8.8 Hz, 2H, ArH), 8.50 (s, 1H, = CH). MS (m/z) = 200 (M + 1).

2.5d Compound (table 2, 3g): IR (KBr, cm⁻¹): 2229, 1584 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): 7.51 (d, 2H, J = 8.5 Hz, ArH), 7.70 (s, 1H, = CH), 7.85 (d, 2H, J = 8.5 Hz, ArH). MS (m/z) = 189 (M + 1).

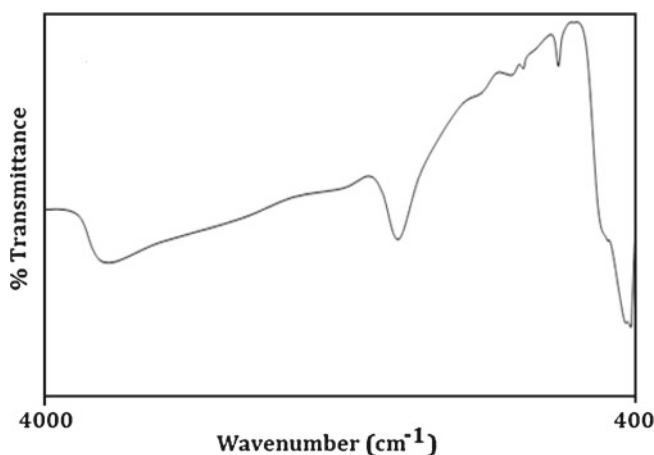
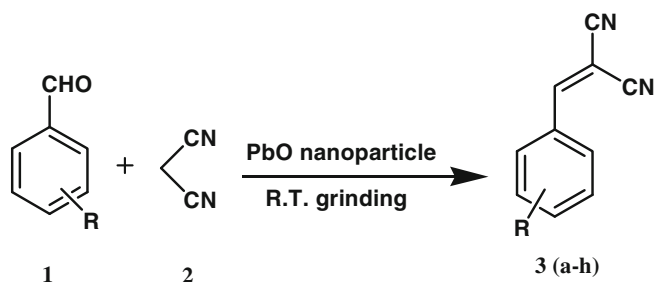


Figure 1. FTIR spectrum of nanocrystalline PbO catalyst.



Scheme 2. Synthesis of benzylidene malonitriles.

3. Results and discussion

The FT-IR spectra of PbO nanoparticles show bands at 574, 642 and 844 cm^{-1} due to Pb–O vibrations (figure 1). The absorption band around 3400 cm^{-1} is due to the presence of water molecules. The XRD pattern (figure 2) suggests that the PbO nanoparticles contain 111, 002, 200, 210, 022, 222, 311 and 131 crystal planes. XRD pattern of the synthesized PbO confirmed the formation of a single orthorhombic structure (JCPDS Card No. 76–1796) with space group $Pca 2_1$ (29). Sharp diffraction peaks indicated good crystallinity. The broadening of peaks indicated that the particles are in nano regime and are in good agreement with observed SEM images. The average particle size of PbO nanoparticles was determined using Debye–Scherer formula⁴¹ and was found to be 69 nm.

The SEM image (figure 3) showed the morphology and size of the synthesized PbO nanoparticles which, suggested the surface of the PbO nanoparticles are spongy and discrete in appearance. The elemental analysis (EDAX) confirmed the material contain Pb and O elements (figure 4). The TEM image revealed that the synthesized PbO material is orthorhombic with several hexagonal shaped crystallites (figure 5). The dark spot in the TEM micrograph (figure 5) can be alluded to

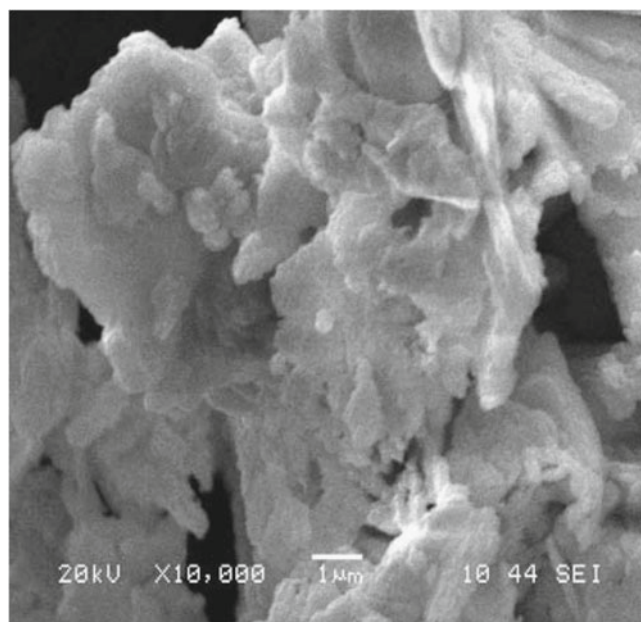


Figure 3. SEM image of nanocrystalline PbO catalyst.

synthesized PbO nanoparticles as SAED pattern associated with such spots reveals occurrence of PbO in total agreement with the XRD data. The average size of the PbO nanocrystallite by TEM was found to be 69 nm.

The N_2 adsorption–desorption isotherms and BJH pore size distribution of PbO nanoparticles (figure 6) revealed that the samples have typical IV N_2 adsorption–desorption isotherms with H_1 hysteresis which indicated that the sample reserve the cylindrical mesopores. The BJH pore size distribution demonstrated that all the samples have a narrow pore diameter range. Based on the N_2 adsorption–desorption isotherms, the specific surface area (S_{BET}) of PbO nanoparticles obtained from BET method was $31.99\text{ m}^2/\text{g}$, the average pore volume (V_p) and pore diameter (dp) were 0.02256 cc/g and 30.86 \AA (figure 6).

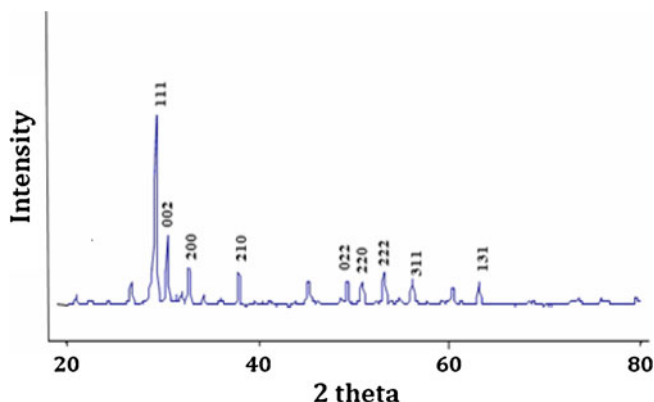


Figure 2. XRD pattern of nanocrystalline PbO catalyst.

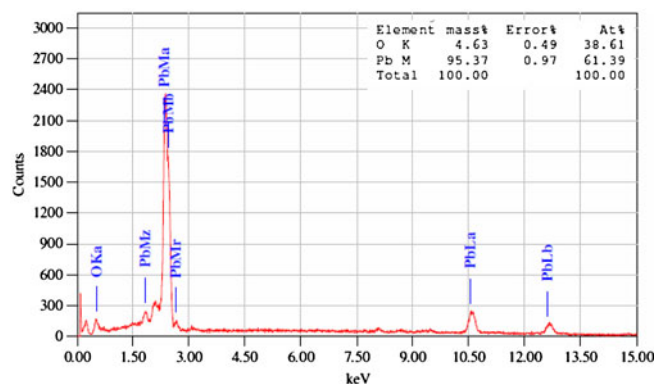


Figure 4. EDAX spectrum of nanocrystalline PbO catalyst.

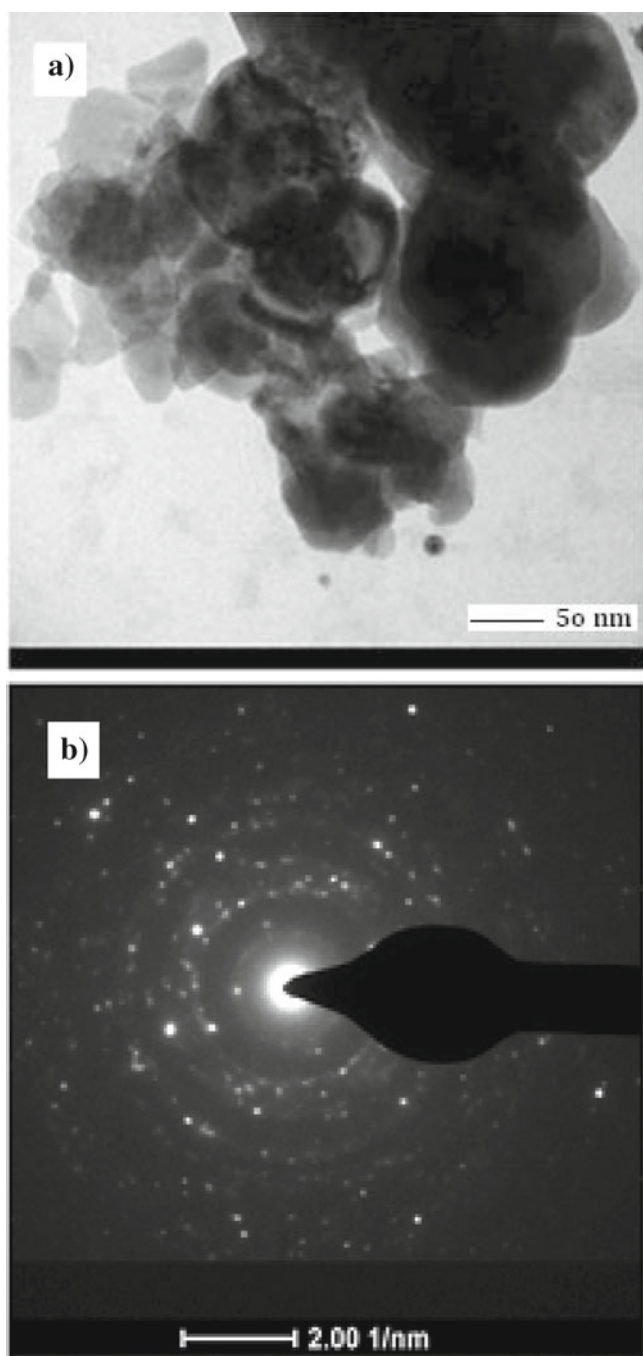


Figure 5. (a) TEM image of nanocrystalline PbO catalyst. (b) SAED image of nanocrystalline PbO catalyst.

3.1 Catalytic results

In continuation of our work on the synthesis of heterocyclic molecules using nanoparticles for cyclization and condensation reactions.^{42,43} We report here facile synthesis of tetrahydrobenzo pyrans and benzylidene malonitriles by grinding under solvent-free condition using PbO nanoparticles. To optimize the reaction condition for synthesis of tetrahydrobenzopyrans, benzaldehyde, malononitrile and dimedone were used as a reactant.

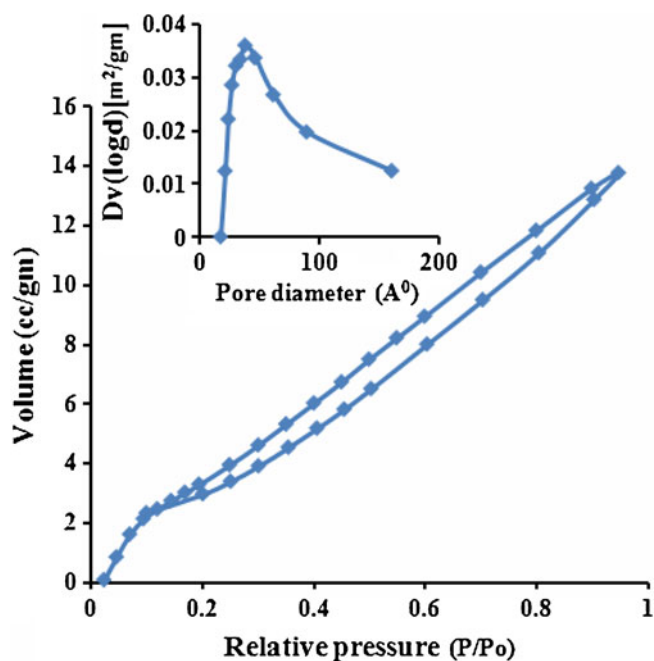


Figure 6. BET surface area and pore size of nanocrystalline PbO catalyst.

In order to verify the role of grinding, the reaction mixture was left over night when it was observed that reaction remained incomplete and in the absence of catalyst does not proceed even after grinding. Under the optimized reaction conditions, a range of substituted tetrahydrobenzo pyran derivatives were synthesized by grinding at room temperature (table 1) using PbO as catalyst. In order to study the scope of the reaction, several substituted aromatic aldehydes with electron-donating as well as electron-withdrawing groups were employed. The reaction proceeded smoothly with good yields. The aromatic aldehydes with hydroxyl group required longer reaction time and gave lower yield. The heterocyclic aldehydes also reacted smoothly to give corresponding derivatives.

Similarly, for the synthesis of benzylidene malonitriles, benzaldehyde and malononitrile were used as model reaction to optimize the reaction condition. As mentioned above, the role of grinding was important for completeness of reaction. Under the optimized reaction conditions a range of substituted benzylidene malonitrile derivatives were synthesized by grinding at room temperature (table 2). The reactions proceeded smoothly for electron-withdrawing and electron-donating aromatic aldehydes with high yields. The aromatic aldehydes with hydroxyl groups and chloro groups at *ortho* position required longer reaction time and gave lower yields. The strong electron-donating aromatic aldehydes reacted quickly with high yields.

Table 3. Effect of amount of catalyst on the reaction.

Entry	Catalyst (mg)	Scheme 1 ^a		Scheme 2 ^b	
		Time (min)	Yield (%)	Time (min)	Yield (%)
1	10	40	61	21	76
2	20	32	63	16	81
3	30	21	75	12	87
4	40	17	81	07	91
5	50	12	83	07	91
6	60	12	83	07	90
7	70	12	83	07	90

^aBenzaldehyde (1.0 mmol), malononitrile (1.0 mmol), dime-done (1.0 mmol) in the presence of catalyst

^bBenzaldehyde (1.0 mmol), malononitrile (1.0 mmol) in the presence of catalyst

The role of catalyst was also studied for the model reaction with different amount of catalysts such as 10, 20, 30, 40, 50, 60 and 70 mg. It was observed that 50 mg of catalyst was sufficient to promote the reaction and greater amount of the catalyst did not improve the yields (table 3). In the synthesis of benzylidene malononitriles, to study the amount of catalyst required, the model reaction of benzaldehyde and malononitrile (scheme 2) was used with different amount of catalysts such as 10, 20, 30, 40, 50, 60 and 70 mg. It was found that the use of 40 mg of the catalyst was sufficient to promote the reaction (table 3).

To study the reusability of catalyst, it was separated after the completion of the reaction, washed with acetone and dried at 100°C and reused in the model reaction for four consecutive runs (table 4). Further, recycled catalyst was characterized by different analytical techniques. We observed that the particle size and crystal morphology of reused PbO nanoparticles was nearly the same. After every use, a little loss of catalytic activity was observed which may be attributed to microscopic change in the structure of the catalyst.

Table 4. Recycling of catalyst.

Reaction	Cycle	1	2	3	4	5
		Fresh	First reuse	Second reuse	Third reuse	Fourth reuse
Scheme 1	Yield (%)	83	81	79	79	71
Scheme 2	Yield (%)	91	90	89	89	80

4. Conclusions

We have developed a convenient, efficient protocol for one-pot synthesis of tetrahydrobenzo pyrans and benzylidene malonitriles in the presence of nanocrystalline PbO catalyst by grinding at room temperature. The attractive features of this procedure are simple work-up, mild reaction condition, short reaction time, excellent yield, solvent-free reaction and utilization of nanoparticles as a reusable catalyst.

Supplementary material

Supplementary material given as figures S1–S5 can be seen online www.ias.ac.in/chemsci website.

Acknowledgements

Authors thank the University Grants Commission (UGC), New Delhi, for financial support, University of Pune, Pune and Sophisticated Analytical Instrument Facility (SAIF) Panjab University, Chandigarh for providing spectral analysis facilities. Authors are also thankful to Prof. A G Gadhave for his helpful suggestions.

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