A green recyclable poly(4-vinylpyridine)-supported copper iodide nanoparticle catalyst for the chemoselective synthesis of pentaerythritol diacetals from aromatic aldehydes

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Poly(4-vinylpyridine)-supported copper(I) iodide nanoparticles have been used as an efficient, green recyclable catalyst for the chemoselective synthesis of pentaerythritol diacetals from aromatic aldehydes and pentaerythritol under solvent-free conditions. This catalyst was reused six times without any loss of its activity.

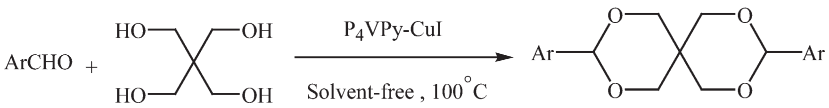
Keywords: poly(4-vinylpyridine)-supported, nanoparticles, copper(I) catalysis, pentaerythritol diacetals, synthetic carbohydrates, steroid chemistry

Acetals are important in synthetic carbohydrate and steroid chemistry. In the phytopharmaceutical, fragrance and lacquer industries acetals are used both as intermediates and as end products. Pentaerythritol diacetals are also used as plasticisers and vulcanisers, physiologically active substances and as protecting groups for aldehydes and ketones.[1–3] Strong protic acids and various Lewis acids have been employed as catalysts for the synthesis of pentaerythritol diacetals.[4–11] However, many of these procedures suffer from one or more of the following disadvantages: toxic solvents, tedious work-up procedure, long reaction times, low yields, corrosive reagents, effluent pollution and non-recyclable catalysts. Therefore, there is scope to develop an alternative method for the synthesis of pentaerythritol diacetals. In recent years, nano-catalysis has emerged as a sustainable and competitive alternative to conventional catalysis since the nanoparticles possess a high surface-to-volume ratio, which enhances their activity and selectivity.[12] Nanomaterials with their large surface area and high density of active sites, are used as heterogeneous catalysts in organic synthesis. In particular, the immobilisation of copper(I) salts on nanoparticles with high-surface-area supports affords a higher stability and dispersion of the particles as well as a further exploitation of the special activity and recycling properties of the catalyst. Recently CuI has emerged as an effective Lewis acid catalyst for various organic transformations.[13–18] However, in spite of its potential application, CuI has some limitations such as thermodynamic instability, long reaction times, non-recyclable, toxicity and difficulty in separation of the product from the reaction medium. Such drawbacks could be obviated by a supported catalyst. Nitrogen-based polymer have been shown to protect the metal centre from oxidation and disproportionation, while enhancing its catalytic activity.[19] To improve the recovery and reuse, copper species have been immobilised on various supports such as carbon,[20] amine-functionalised polymers,[21] zeolites,[22] amine-functionalised silica and aluminum oxide/hydroxide fibre.[23–24] Poly(4-vinylpyridine)-supported reagents are active in various organic reactions including oxidations, reductions and halogenations. Simple recovery from reaction mixtures, their reusability, compatibility with a wide range of solvents, physical stability, and their toleration of a great number of reaction conditions bodes well for the future of P_4VPy-supported reagents where their properties can be fine-tuned for specific chemical transformations.[25] Recently, we have reported the preparation of copper iodide nanoparticles supported on poly(4-vinylpyridine) (P_4VPy–CuI) and their application for the click synthesis of triazole derivatives.[26–27] In continuation of these studies, we now report the application of this reagent to the chemoselective synthesis of pentaerythritol diacetals from aromatic aldehydes under solvent-free conditions (Scheme 1).

Results and discussion

The copper(I) iodide catalyst immobilised on poly(4-vinylpyridine), was readily prepared in a one-step procedure. Poly(4-vinylpyridine) was refluxed with a solution of CuI under a N_2 atmosphere in EtOH for the synthesis of polymer-supported CuI nanoparticles. This method was developed for the effective synthesis of copper nanoparticles incorporated heterogeneously as a catalyst in some organic reactions. [28] Optimisation of the reaction conditions showed that the best results were obtained under solvent-free conditions, in the presence of 0.1 g of P_4VPy–CuI at 100 °C when the relative ratio of the substrate to pentaerythritol was 2:1, respectively. A wide range of various aromatic aldehydes were then successfully reacted to afford the desired products. Among the various substrates which were studied, compounds containing electron-withdrawing groups were found to be the most reactive and were converted to the corresponding products in shorter reaction times. (Table 1, entries 4, 8 and 9). Because ketones were unreactive under these conditions (Table 1, entries 16 and 17), the reported method can be used for the chemoselective acetalisation of aldehydes in the presence of ketones (Table 1, entry 18).

The activity of the recovered catalyst was also examined under the optimised conditions and the desired product was obtained in high yields after 1–6 runs (Table 2) using the reaction of benzaldehyde with pentaerythritol as the model (Table 2). After the reaction was completed the P_4VPy–CuI was washed with ethylacetate, dried and stored for another reaction. This process was repeated for six runs and no appreciable decrease in the yield was observed. Next we checked the leaching of CuI into the reaction mixture from the poly(4-vinylpyridine) support using ICP-AES. The difference between the copper content of the fresh and reused catalyst (sixth run)



Scheme 1 Synthesis of pentaerythritol diacetals catalysed by P_4VPy–CuI.

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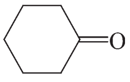
Table 1 P_4VPy–CuI catalysed synthesis of pentaerythritol diacetals

Entry	Substrate	Time /min	Yield /%[a]	M.p./°C[b]	
				Found	Reported[7–11]
1	PhCHO	25	95	153–154	155–156
2	2-ClPhCHO	20	93	140–141	141–142
3	3-ClPhCHO	25	92	120–122	121–122
4	4-ClPhCHO	20	92	198–200	196–197
5	3-MePhCHO	25	91	189–191	190–191
6	4-MePhCHO	30	92	209–211	211–212
7	2-NO_2PhCHO	25	94	163–165	162–164
8	3-NO_2PhCHO	25	93	183–185	185–186
9	4-NO_2PhCHO	15	93	226–228	226–227
10	4-MeOPhCHO	60	86	180–182	180–182
11	4-HOPhCHO	60	85	109–111	108–110
12	2-HOPhCHO	50	86	160–162	160–161
13	4-BrPhCHO	25	89	221–223	222–224
14	2-Furaldehyde	45	85	157–159	157–159
15	4-Me_2NPhCHO	60	87	223–224	223–224
16		45	0[c]	–	111–113
17	Ph_2CO	60	0[c]	–	163–164
18	PhCHO + Ph_2CO	30	100[d] + 0[d]	153–154	155–156

[a] Isolated yield. [b] Products were characterised by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature[7–11]. [c] Starting material recovered intact. [d] Conversion.

Table 2 Re-use of P_4VPy–CuI

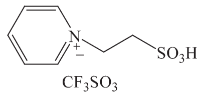
Run	1	2	3	4	5	6
Time/min	25	25	28	30	40	45
Yield/%[a]	95	95	93	93	90	90

[a] Isolated yield

was only 4% which indicates a low leaching of the copper iodide catalyst into the reaction mixture.

In order to demonstrate the efficiency of this method, Table 3 compares the results from the acetalisation of benzaldehyde in the presence of P_4VPy–CuI and some other catalysts. In comparison with previously reported methods, our catalyst promoted the reaction very effectively, and gave the desired product in a very short time with a high yield. Very low amounts of the catalyst were needed. This catalyst is cheap, easy to handle and its preparation is simple and straightforward. It can be recovered simply by filtration and it can be reused in further runs without a significant decrease in yield of the products. Moreover, our procedure is environmentally friendly as it does not use any toxic auxiliary or solvent.

Table 3 Comparison of the efficiency of P_4VPy–CuI in the synthesis of pentaerythritol diacetal from benzaldehyde, with other reported methods.

Entry	Reagent	Conditions	Time /min	Yield /%[a]	Ref.
1	$H_3PW_{12}O_4$	Toluene/reflux	120	92	9
2		100 °C	90	91	11
3	NH_2SO_3H	Toluene/110 °C	240	96	7
4	$H_3PW_{12}O_4$ suported on MCM-41	Toluene/reflux	120	92	10
5	$FeSO_4$	Benzene/reflux	90	97	8
6	P_4VPy–CuI	Solvent-free /100 °C	25	95	This work

[a] Isolated yield

In conclusion, we have descibed a new, green and efficient procedure for the chemoselective synthesis of pentaerythritol diacetals catalysed by P_4VPy–CuI under solvent-free conditions. This catalytic system is stable and can promote the yields and reaction times over six runs without loss of activity. Moreover, the heterogeneous reaction conditions, high yields of products, short reaction times, ease of work-up and clean procedure, could make this procedure a useful addition to the available methods.

Experimental

Chemicals were purchased from the Fluka, Merck and Aldrich Chemical Companies .All the products were characterised by comparison of their spectroscopic data (^1H NMR and IR) and physical, properties with those reported in the literature. The IR spectra were recorded on a Perkin-Elmer 781 Spectrophotometer. All the NMR spectra were recorded on a Bruker Avance 400 MHz. Melting points were recorded on a Bransted Electro thermal 9100BZ melting point apparatus. Yields refer to isolated pure products.

General procedure

A mixture of the aldehyde (2 mmol), pentaerythritol (1 mmol) P_4VPy–CuI (0.1 g) was heated in an oil bath (100 °C) for the appropriate time (Table 1). After completion of the reaction, as shown by TLC, the reaction mixture was cooled to room temperature and ethyl acetate (5 mL) was added to the mixture which was filtered. The catalyst was washed with ethyl acetate, dried and stored for another reaction run. Evaporation of the solvent from the filtrate and recrystallisation of the solid residue from hot ethanol afforded the pure products in high yields.

We thank the Behbahan Khatam Alanbia University of Technology for partial support of this work.

Received 12 July 2012; accepted 11 August 2012
Paper 1201410 doi: 10.3184/174751912X13460806564901

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