

PEI–Silica Catalysis Under Microwave Irradiation: Solvent-Free Condensation of Dehydroacetic Acid with Aromatic and Heteroaromatic Aldehydes [†]

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Abstract

Polyethylenimine supported on silica (PEI–SiO₂) is an efficient heterogeneous catalyst for the Knoevenagel condensation of dehydroacetic acid (DHA) with aromatic and heteroaromatic aldehydes. The combination of the basic PEI phase with the acidic silanol groups of silica provides an acid–base cooperative catalytic system and gives higher activity than PEI alone under the conditions examined. Microwave irradiation enables the condensations to be performed under solvent-free reaction conditions within short reaction times. The solid catalyst can be readily recovered, washed, and reused for at least five cycles, with isolated yields remaining in the 90–94% range for the model reaction. The method was applied to a broad set of aromatic and heteroaromatic aldehydes, affording the corresponding 4-hydroxy-6-methyl-3-(arylacryloyl)-2H-pyran-2-ones.

Keywords: dehydroacetic acid (DHA); polyethylenimine (PEI); PEI–SiO₂; 2H-pyran-2-one; Knoevenagel condensation; acid–base cooperative catalysis; microwave irradiation; solvent-free synthesis; catalyst recycling

1. Introduction

Dehydroacetic acid (DHA; 3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) is a versatile synthetic building block, and derivatives of DHA are associated with a broad range of biological activities [1]. DHA can be prepared readily from ethyl acetoacetate [2]. The methyl group of the acetyl substituent is sufficiently acidic to undergo Knoevenagel-type condensation with aldehydes in the presence of acid–base catalysts. Early examples employed piperidine as a basic catalyst in chloroform [3], while other acid–base catalytic systems have subsequently been described. Rehse reported the use of the PTS–pyridine pair as an efficient catalytic system [4].

The aim of the present study was to evaluate polyethylenimine supported on silica (PEI–SiO₂) as a recyclable heterogeneous catalyst [5] for the condensation of DHA with aromatic and heteroaromatic aldehydes. The study first compares representative acidic, basic, and acid–base catalysts under conventional heating, then examines the effect of catalyst loading and microwave irradiation [6], evaluates catalyst recycling, and finally explores the substrate scope.



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2. Results and Discussion

2.1. General

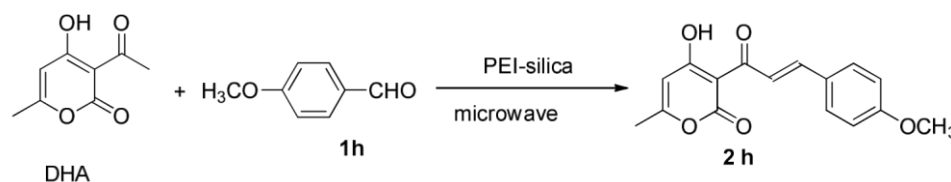
Microwave-irradiation reactions were performed with monomode microwave apparatus Synthewave 402 microwave reactor (Prolabo, Paris, France) operating at 2450 MHz.

NMR spectra were recorded at 400 MHz for ^1H NMR and 100.6 for ^{13}C NMR with a Bruker AC 400 spectrometer (Rheinstetten, Germany) with CDCl_3 as solvent and TMS as an internal standard.

PEI was BASF (Ludwigshafen, Germany) product and reagents were obtained from Aldrich (St. Louis, MO, USA).

2.2. Catalyst Screening

As an initial screening experiment, the condensation of p-anisaldehyde (Ar = C₆H₄–4 OCH₃) with DHA was examined in the absence of solvent under conventional heating at 100 °C (Scheme 1). Product formation was quantified by ¹H NMR spectroscopy using anisole as the internal standard.



Scheme 1. Condensation of p-anisaldehyde with DHA.

The catalyst classes examined were as follows:

1. Basic catalysts: butylamine (>75% conversion), polyethylenimine (PEI, 50%), pyridine (0%), and piperidine (50%).
2. Acidic catalysts: boric acid (30%) and camphorsulfonic acid (55%).
3. Acid–base catalysts: sulfamic acid (40%), β -alanine (55%), and PEI supported on silica (PEI-SiO₂, >75%).

Butylamine and PEI-SiO₂ gave the highest conversion among the catalysts tested.

Several other catalysts led to incomplete conversion and/or by-products. PEI alone was less active than PEI-SiO₂ under the same conditions. The higher activity of the supported material may result from cooperative interactions between the basic amine functions of PEI and the acidic silanol groups present at the silica surface.

2.3. Microwave Activation

In this communication, we describe the use of PEI-SiO₂ in the condensation of dehydroacetic acid with aromatic aldehydes under microwave irradiation without solvent and with short reaction times. Under these conditions, the syntheses are consistent with green-chemistry principles. The condensation of p-anisaldehyde with DHA was investigated under microwave irradiation; the optimum conditions were 359 W for 15 min.

2.4. Catalyst Recycling

The reusability of PEI-SiO₂ was investigated for five consecutive cycles using the 29 Knoevenagel condensation of p-anisaldehyde (1 h) with DHA under microwave irradiation (350 W, 15 min). After each cycle, the catalyst was recovered, washed with acetonitrile, and characterized by FT-IR spectroscopy. No significant changes were observed in the FT-IR spectrum after five cycles.

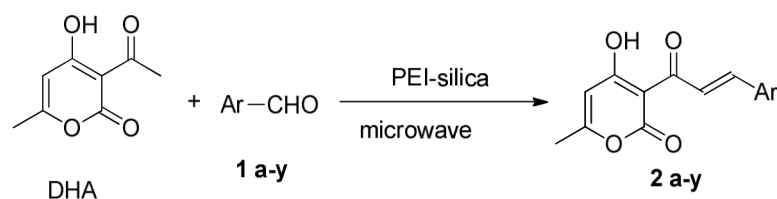
The isolated yield remained between 90% and 94% over the five cycles (Table 1), indicating that the catalyst retains a high level of activity under the recycling conditions 35 examined. Conversion values from the catalyst-screening experiments are therefore 36 distinguished here from the isolated yields reported for recycling.

Table 1. Results obtained using recycled PEI-SiO₂ catalyst.

Reaction Cycle	Isolated Yield (%)
1	94
2	94
3	91
4	90
5	90

2.5. Substrate Scope

The scope of the reaction was examined with a range of aromatic and heteroaromatic aldehydes (1a–w) in the presence of PEI-SiO₂ under microwave irradiation (Scheme 2). The substrates include electron-donating groups (OMe, SMe, iPr), electron-withdrawing groups (NO₂, CN), halogens, hydroxy substituents, and heteroaromatic rings (pyridyl, furyl, and thienyl). The corresponding 4-hydroxy-6-methyl-3-(arylacryloyl)-2H-pyran-2-ones were characterized by ¹H and ¹³C NMR spectroscopy, IR spectroscopy, mass spectrometry, and melting-point analysis, as appropriate. Literature melting points are reported in Table 2 for comparison [7–12].



Scheme 2. Condensation of DHA with aromatic and heteroaromatic aldehydes.

Table 2. Condensation of DHA with aromatic and heteroaromatic aldehydes using PEI-SiO₂ under microwave irradiation.

No.	R	Yield (%)	mp (°C)	Literature mp (°C)	Ref.
a	H	70	131	130–132	7
b	2-Cl	80	123	122–124	8
c	2-OMe	73	178	177–179	9
d	2-NO ₂	90	170	171	8
e	2-OH	40	208	208	10
f	3-NO ₂	85	111	112	10
g	4-Cl	73	158	159	8
h	4-OMe	47	208	208–209	11
i	4-NO ₂	93	245	245	13
j	4-CN	89	236	235	7
k	4-OH	40	233	235	10
l	4-Br	73	128	128–129	12
m	4-SMe	64	192	195	9

Table 2. Cont.

No.	R	Yield (%)	mp (°C)	Literature mp (°C)	Ref.
n	4-iPr	52	140	139–141	7
o	2,4-Cl	73	154	155–156	5
p	3,4-OMe	66	185	185	7
q	3,4,5-OMe	57	125	125–126	9
r	2,3-OMe	66	147	147	7
s	2-Pyridyl	45	160	160–161	pat
t	2-Furyl	62	144	144	3
v	2-Thienyl	52	165	165	3
w	4-Pyridyl	90	166	167	12
y	3,4-OCH ₂ O	94	190	189	7

Conditions: 350 W, 3–20 min. Most products were obtained predominantly as the E isomer (>98%). The exceptions were compound 2 (Z/E = 3:4) and compound 4 (Z/E = 2:5). The close 16 agreement between the experimental and literature melting points supports the assigned product identities.

3. Experimental

3.1. Preparation of PEI–SiO₂ (20:1 Silica/PEI, w/w)

Silica gel (Merck Grade 7734; 70–230 mesh; particle size 63–200 µm; 20 g) was 21 added to a solution of polyethylenimine (PEI; molecular weight approximately 2,000,000) prepared from 4.2 g of an aqueous 24 wt% PEI solution (corresponding to approximately 1.0 g of PEI) in ethanol (40 mL). After stirring, the solvent was removed under reduced pressure to give a white, free-flowing powder.

3.2. Catalyst-Screening Experiment

DHA (2.5 mmol), p-anisaldehyde (2.5 mmol), and anisole (0.2 mmol) as the internal standard were combined with the appropriate catalyst in individual test tubes. The tubes were heated on a hot plate at up to 100 °C for 2 h. After cooling, the products were analyzed by ¹H NMR spectroscopy.

3.3. Recycling of PEI–SiO₂

After each reaction cycle, the PEI–SiO₂ catalyst was recovered, washed, and dried before reuse. The recycled catalyst was analyzed by FT-IR spectroscopy; the reported bands were 1592.2 cm^{−1} (N–H) and 1063.1, 786.3, and 662.6 cm^{−1} (Si–O–Si). No significant changes were observed after five cycles. The isolated product yield remained in the range of 90–94% over five cycles (Table 1).

3.4. General Procedure for the Condensation of DHA with Aromatic Aldehydes

DHA (5 mmol) and the aldehyde (5 mmol) were adsorbed onto 3 g of PEI–SiO₂ catalyst. The mixture was irradiated at 350 W for 3–20 min with a Synthewave (Prolabo), depending on the substrate. Reaction progress was monitored by removing a small sample of the solid, extracting it with acetonitrile (1 mL), and analyzing the extract by thin-layer chromatography (TLC). After completion, irradiation was stopped and the product was extracted by elution with dichloromethane or acetonitrile. The solvent was removed under reduced pressure. The crude product was recrystallized from ethanol or purified by flash chromatography on silica gel. Product identity was assessed by ¹H and ¹³C NMR

spectroscopy, IR spectroscopy, mass spectrometry, melting point, and TLC Rf comparison with authentic samples, as available.

4. Conclusions

PEI-SiO₂ is readily prepared from commercially available materials and functions as an efficient recyclable heterogeneous catalyst for the Knoevenagel condensation of DHA with aromatic and heteroaromatic aldehydes. Under microwave irradiation, the reaction can be performed under solvent-free conditions in short reaction times. The catalyst retained high activity over five recycling cycles for the model reaction. The substrate scope demonstrates that the method can be applied to a diverse set of substituted aromatic and heteroaromatic aldehydes. The proposed acid–base cooperative effect of PEI and silica provides a plausible explanation for the higher activity of the supported catalyst, although a more detailed mechanistic study would be required to establish this point definitively.

Overall, the results support PEI-SiO₂ as a practical recyclable catalyst for solvent-free Knoevenagel condensations of DHA under microwave irradiation.

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