# ORIGINAL PAPER

# ZSM-5-SO<sub>3</sub>H as a novel, efficient, and reusable catalyst for the chemoselective synthesis and deprotection of 1,1-diacetates under eco-friendly conditions

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**Abstract** ZSM-5 has been modified as supported sulfuric acid (ZSM-5-SO<sub>3</sub>H) and introduced for the first time as a mild, convenient, reusable, and heterogeneous catalyst. Various types of aldehydes were efficiently converted to their 1,1-diacetates using a catalytic amount of ZSM-5-SO<sub>3</sub>H in excellent yields under solvent-free and heterogeneous conditions at room temperature. The deprotection of 1,1-diacetates has also been achieved using this novel catalyst in ethanol. The procedure is operationally simple, environmentally benign, and only a stoichiometric amount of anhydride is used.

#### Introduction

The electrophilic nature of carbonyl groups is a dominant feature of their extensive chemistry. One of the major challenging problems during many multi-step syntheses is how to protect a carbonyl group from nucleophilic attack until its electrophilic properties can be exploited. Acetylation is commonly utilized as a protecting method for carbonyl functions, because 1,1-diacetates are stable against

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A. R. Massah · R. J. Kalbasi Razi Chemistry Research Center, Shahreza Branch, Islamic Azad University, 86145-311, Shahreza, Isfahan, Iran a wide range of nucleophiles under neutral and basic conditions [1, 2]. Moreover, they are also used as substrates for nucleophilic substitution reactions [3-7]. 1,1-Diacetates of  $\alpha,\beta$ -unsaturated aldehydes are important precursors for acetoxy dienes [8] and dihalovinyl acetates [9]. Therefore, methods for their synthesis have received considerable attention. Usually, they are prepared from aldehydes and acetic anhydride using sulfuric [10], methanesulfonic [11], or perchloric acid [12], although the yields in many cases are poor. Also, several methods have been developed for the preparation of 1,1-diacetates by employing various Lewis acids such as Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O [13], cupric sulfate [14], In(OTf)<sub>3</sub> [15], P<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> [16], LiOTf [17], Bi(NO<sub>3</sub>)<sub>3</sub> [18], Keggin heteropolyacid [19], Al(HSO<sub>4</sub>)<sub>3</sub> [20], titaniummodified MCM-41 [21], sulfuric acid [3-(3-silicapropyl) sulfanyl]propyl ester [22], silica-bonded N-propylsulfamic acid [23], polymer-supported gadolinium triflate [24], different solid acids [25], and Brønsted acidic ionic liquids under ultrasonic irradiation [26]. However, many of these existing methodologies suffer from one or more of the following disadvantages: prolonged reaction times and low yields [13], high temperatures [19], use of harmful organic solvents [19, 27, 28], use of moisture-sensitive and costly catalysts (e.g., triflates) [15, 24], and use of excess Ac<sub>2</sub>O [29]. Also, very few reports are applicable to both the synthesis as well as deprotection of 1,1-diacetates [30-32].

Solvent-free organic synthesis for the preparation of small molecule libraries is now routinely applied in pharmaceutical research for the discovery and optimization of lead compounds [33–37]. On the other hand, solid supported reagents are unique catalysts that have become popular recently [38–41]. The high catalytic activity, low toxicity, moisture and air tolerance, recyclability, and particularly their low price make the use of solid supported reagents an attractive alternative to conventional acids.

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Scheme 1

R = CI, Br, Me, MeO, NO<sub>2</sub>, OH, H

Some of the solid supported acids, e.g.,  $SiO_2-OSO_3H$  [29] and  $HClO_4-SiO_2$  [42], are utilized as catalysts for the preparation of 1,1-diacetate derivatives from the corresponding aldehydes. Recently, we have demonstrated the applicability of  $SiO_2-OSO_3H$  [43],  $H_3PO_4/TiO_2-ZrO_2$  [44, 45],  $H_3PO_4/ZSM-5$  [46],  $SiO_2-OPO_3H$  [47], and  $SiO_2-Cl$  [48] as solid supported acids in several organic transformations.

In continuation of our studies we have found that ZSM-5 reacts with chlorosulfonic acid to give a white powder, which was shown as ZSM-5-SO<sub>3</sub>H. It is interesting to note that the reaction is easy and clean without any work-up procedure, because HCl gas is evolved from the reaction vessel immediately [38]. However, we hope that ZSM-5-SO<sub>3</sub>H would be a good proton source as well as other reported solid supported acids or acidic resins, such as SSA, polystyrene sulfonic acid, and Nafion-H [49]. Herein, we introduce ZSM-5-SO<sub>3</sub>H as a reusable catalyst for the synthesis of 1,1-diacetates from structurally diverse aldehydes under mild and solvent-free conditions (Scheme 1).

#### **Results and discussion**

#### Characterization of the catalyst

Initially, a systematic study was carried out for the preparation and characterization of different ZSM-5 supported SO<sub>3</sub>H. The infrared spectra of ZSM-5 and the samples with various amounts of ClSO<sub>3</sub>H supported on ZSM-5 are presented in Fig. 1. In the sample Na-ZSM-5 the broad peaks in the range of  $3,200-3,600 \text{ cm}^{-1}$  may be attributed to the hydroxyl stretching of hydrogen-bonded internal silanol groups and O-H stretching of water, while the peak at  $1,620-1,640 \text{ cm}^{-1}$  corresponds to bending mode of O–H of water. Beside those, the peaks around 800 and  $1,090 \text{ cm}^{-1}$ are attributed to the symmetric and asymmetric stretching vibrations of the Si-O-Si groups, respectively [50]. The band at  $470 \text{ cm}^{-1}$  is assigned to the bending vibrations of Si-O-Si or Al-O-Si groups [51]. In the samples with various amounts of ClSO<sub>3</sub>H loaded on ZSM-5 some additional peaks were observed. The asymmetric and symmetric stretching of the S=O bond at 1,229-1,290 and  $1,177 \text{ cm}^{-1}$ , respectively, confirms the presence of SO<sub>3</sub>H in CISO<sub>3</sub>H/ZSM-5 [52, 53]. The other peaks in the range of 750–1,000  $\text{cm}^{-1}$  were attributed to the S–O bond. It should be mentioned that with increasing the ClSO<sub>3</sub>H loaded on



**Fig. 1** FT-IR spectra of *a* Na-ZSM-5 and ClSO<sub>3</sub>H/ZSM-5 catalysts with *b* 15 wt% ClSO<sub>3</sub>H, *c* 20 wt% ClSO<sub>3</sub>H, *d* 28 wt% ClSO<sub>3</sub>H, and *e* 34 wt% ClSO<sub>3</sub>H

the ZSM-5, the intensity of the peaks related to S=O and S–O increases.

XRD powder patterns of the calcinated samples of ZSM-5 and ZSM-5-SO<sub>3</sub>H with different amounts of loaded chlorosulfonic acid are presented in Fig. 2. Figure 2a shows reflections at  $2\theta$  values of 7–9 and 23–25°, which agree well with the characteristic peak of MFI structure, indicating the synthesized composite material ZSM-5 zeolite crystal. The ZSM-5-SO<sub>3</sub>H samples showed the same pattern, indicating that the ZSM-5 framework was well retained after immobilizing. However, the intensity of the characteristic reflection peaks of ZSM-5-SO<sub>3</sub>H samples is found to be reduced to some extent. This may be attributed to the X-ray shielding caused by absorption of non-metal material after acid loading over the zeolite samples. A similar observation has been reported by Breck [63]. In addition, the composite contains much less ZSM-5



Fig. 2 XRD powder patterns of the calcinated samples of zeolite ZSM-5 catalysts containing different amounts of loaded chlorosulfonic acid:  $a \ 0\%$ ,  $b \ 15\%$ ,  $c \ 20\%$ ,  $d \ 28\%$ ,  $e \ 34\%$ 



Fig. 3 Nitrogen adsorption-desorption analysis of ZSM-5 zeolite with various amounts of loaded chlorosulfonic acid: a 15%, b 20%, c 28%, d 34%

because of the dilution of the silicious material by CISO<sub>3</sub>H; therefore, this dilution can also account for a decrease in the peak intensity.

The N<sub>2</sub> adsorption–desorption isotherms of ZSM-5-SO<sub>3</sub>H (15%) (a), ZSM-5-SO<sub>3</sub>H (20%) (b), ZSM-5-SO<sub>3</sub>H (28%) (c), and ZSM-5-SO<sub>3</sub>H (34%) (d) samples are shown in Fig. 3. The isotherms are similar to the type III isotherm with H1-type hysteresis loops at high relative pressure according to the IUPAC classification, characteristic of microporous materials. The specific surface area and the pore size have been calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

The structure data of all these materials (BET surface area, total pore volume, and pore size) are summarized in

 Table 1
 Porosity data of ZSM-5 and ZSM-5-SO<sub>3</sub>H synthesized with different amounts of chlorosulfonic acid

Sample/%	BET surface area/m <sup>2</sup> g <sup><math>-1</math></sup>	$V_{\rm P}/{\rm cm}^3~{\rm g}^{-1}$	D <sub>P</sub> /nm
ZSM-5	375	-	-
ZSM5-SO <sub>3</sub> H (15)	345	2.07	0.18
ZSM5-SO <sub>3</sub> H (20)	286	2.21	0.16
ZSM5-SO <sub>3</sub> H (28)	122	2.01	0.068
ZSM5-SO <sub>3</sub> H (34)	119	2.29	0.065

Table 1. It is known that ZSM-5 has a high BET surface area (375 m<sup>2</sup> g<sup>-1</sup>), indicative of its potential application as a host in inorganic materials. BET surface areas of ZSM-5-SO<sub>3</sub>H samples are smaller than ZSM-5. After modification with ClSO<sub>3</sub>H, ZSM-5-SO<sub>3</sub>H samples exhibit a lower BET surface area in comparison with those of pure ZSM-5 zeolite, which might be due to the presence of SO<sub>3</sub>H groups on the pore surface. In addition, the pore volume decreased with increasing the amount of loaded chlorosulfonic acid. This means that the chlorosulfonic acid is uniformly grafted onto the pore wall surface of ZSM-5-SO<sub>3</sub>H zeolite materials.

Figure 4 shows the SEM images of the ZSM-5 zeolite and ZSM-5-SO<sub>3</sub>H (28%). In Fig. 3a, it can be seen clearly that the ZSM-5 crystal with a size of about 10  $\mu$ m was successfully synthesized, and the morphology of synthesized ZSM-5 crystal was spherical-like.

After loading the  $CISO_3H$  on ZSM-5, spherical-like particles remained. So the morphology of the catalyst did not change, and it can be concluded that the ZSM-5-SO<sub>3</sub>H is a stable catalyst with preservation of ZSM-5 crystallinity (Fig. 4b).

#### Synthesis and deprotection of 1,1-diacetates

A variety of reaction conditions were performed to optimize the acylation of aldehydes. At first, we tried the conversion of 4-methoxybenzaldehyde to the corresponding 1,1-diacetate with acetic anhydride in various solvents and also under solvent-free conditions in the presence of 0.02 g of ZSM-5-SO<sub>3</sub>H (28%) (Table 2). CH<sub>2</sub>Cl<sub>2</sub> afforded the minimum amount of side products in high yield, and so it was selected as solvent of choice (Table 2, entries 1-4). In comparison, the yield of the product under solvent-free conditions is higher, and the reaction time is lower. For optimization of the quantity of acetic anhydride required for the reaction, we altered the stoichiometry of the reaction. When a 1:1 ratio of 4-methoxybenzaldehyde to acetic anhydride was tried, the reactions were completed in 4-6 min in good to excellent yields (85-95%) in both CH<sub>2</sub>Cl<sub>2</sub> and solvent-free conditions, and no further increase in the yield was observed even after increasing the amount



Fig. 4 Scanning electron microscopy (SEM) photographs of a ZSM-5 and b ZSM-5-SO<sub>3</sub>H (28%)

**Table 2** Conversion of 4-methoxybenzaldehyde to 1,1-diacetateunder different conditions

Entry	Solvent	Ac <sub>2</sub> O/eq	ZSM-5-SO <sub>3</sub> H/g	Time/ min	Yield/ % <sup>a</sup>
1	Ethyl acetate	1	0.02	10	50
2	<i>n</i> -Hexane	1	0.02	10	70
3	CH <sub>3</sub> CN	1	0.02	10	65
4	$CH_2Cl_2$	1	0.02	6	85
5	$CH_2Cl_2$	3	0.02	6	88
6	Solvent-free	1	0.02	4	95
7	Solvent-free	3	0.02	4	95
8	Solvent-free	1	0.01	4	82
9	Solvent-free	1	0.005	4	70
10	CH <sub>2</sub> Cl <sub>2</sub>	3	-	24 h	0
11	Solvent-free	3	-	24 h	0

Room temperature

<sup>a</sup> Yields of isolated products

of acetic anhydride to three or more equivalents (Table 2, entries 4–7). Hence, we maintained a 1:1 stoichiometry throughout the reaction. To illustrate the need for catalysts

for these reactions, an experiment was conducted in which the reaction of 4-methoxybenzaldehyde and acetic anhydride was studied in the absence of ZSM-5-SO<sub>3</sub>H. No reaction occurred even after 24 h in the absence of the catalyst (Table 2, entries 10, 11). Obviously, the catalyst is an essential component of the reaction. Then, a similar reaction was studied in the presence of various amounts of catalyst. We observed that the reaction between 4-methoxybenzaldehyde (1 mmol), acetic anhydride (1 mmol), and ZSM-5-SO<sub>3</sub>H (0.02 g) was completed after 4 min in solvent-free conditions at room temperature. Next, the conversion of 4-methoxybenzaldehyde to the corresponding diacetate was carried out at room temperature using various ZSM-5 supported sulfuric acids, including ZSM-5-SO<sub>3</sub>H (15%), ZSM-5-SO<sub>3</sub>H (20%), and ZSM-5-SO<sub>3</sub>H (34%), resulting in 50, 70, and 70% yields, respectively. However, the best yield of product (95%) was obtained when ZSM-5-SO<sub>3</sub>H (28%) was used as catalyst.

To demonstrate the versatility and uniqueness of the present reaction conditions, a variety of aliphatic as well as aromatic aldehydes were converted into corresponding 1,1-diacetates 1a-1m in high yields (90-98%) at ambient temperature and under solvent-free conditions. Several examples illustrating the usefulness of this efficient and rapid procedure for the preparation of 1,1-diacetates are summarized in Table 3. Various functional groups were tolerated under the present conditions, for example, Me, Cl, OMe, NO<sub>2</sub>, OH, and Br. It is noteworthy to mention that aldehydes with electron withdrawing groups like nitrobenzaldehydes (Table 3, entries 3-5) and acid-sensitive substrates like butenal (Table 3, entry 14) and 2- furfuraldehyde (Table 3, entry 12) gave the corresponding 1,1-diacetates in high yields without formation of any side products. However, when the reaction was extended towards hydroxybenzaldehydes (Table 3, entry 10) under the present reaction conditions, it gave a mixture of products. Ketones proved completely resistant to acylal synthesis with acetic anhydride: no diacetate formed even under reflux conditions (Table 3, entries 15, 16). This prompted us to check and extend the present protocol for chemoselective synthesis of 1,1-diacetate of an aldehyde in the presence of ketone. Using this catalytic system, the highly selective conversion of aldehydes was observed (Scheme 2). In addition, the acylation of 4-methylbenzaldehyde versus 4-nitrobenzaldehyde and 3-nitrobenzaldehyde in the presence of one equivalent of acetic anhydride has been investigated in solvent and solvent-free conditions. These reactions also proceeded with high selectivity in the presence of this catalyst and showed the importance of electronic effects upon these reactions. On the other hand, comparison between the results obtained in solution and those under solventfree conditions show that reactions proceeded faster in

Table 3 ZSM-5-SO<sub>3</sub>H catalyzed protection of aldehydes as 1,1-diacetates and deprotection at room temperature

Entry	Substrate	Protection			Prod.	M.p./°C or b.p./°C (mbar)		Deprotection		
		Solvent-free		CH <sub>2</sub> Cl <sub>2</sub>		Found R	Reported	Time/min	Yield/% <sup>b</sup>	
		Time/min	Yield/% <sup>b</sup>	Time/min	Yield/% <sup>b</sup>					
1	СНО	1	95	4	50	1a	44-45	44-45 [29]	60	85
2	СІ	2	98	2	60	1b	58	58-60 [61]	60	88
3 <sup>a</sup>	NO2 СНО	4	96	4	70	1c	89	91 [16]	30	98
4 <sup>a</sup>	O <sub>2</sub> N-CHO	4	97	4	97	1d	124	124–125 [29]	30	98
5 <sup>a</sup>	О <sub>2</sub> N Сно	4	96	4	80	1e	64	64-65 [29]	30	98
6	Br————————————————————————————————————	2	90	4	80	1f	89	90–91 [29]	30	80
7	н₃с-∕_сно	1	97	2	90	1g	80-81	81 [16]	60	90
8	н₃со-	4	95	6	85	1h	65	64-65 [29]	40	90
9	осн <sub>3</sub>	1	98	5	70	1i	66–67	66–68 [29]	40	80
10	ОН СНО	20	30	20	0		-	-	-	-
11	H₃C H	1	97	2	40	1j	71–73 (20)	73–75 (20) [62]	10	98
12	Н	1	98	2	30	1k	50	51–52 [16]	40	80

Entry	Substrate	Protection		Prod.	M.p./°C or b.p./°	<sup>o</sup> C (mbar) Deprotection		on		
		Solvent-free		$CH_2Cl_2$		Found	Reported	Time/min	Yield/% <sup>b</sup>	
		Time/min	Yield/% <sup>b</sup>	Time/min	Yield/% <sup>b</sup>					
13	∧ → H	1	95	2	55	11	Colorless liquid	128–129 (3) [60]	10	98
14	Н₃С∕СНО	1	95	2	60	1m	93–94 (23)	89–90 (20) [62]	10	98
15	CH3	30	0	30	0		-	_	-	-
16	°,	30	0	30	0		-	-	_	-

Products were confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, and direct comparison with authentic samples

<sup>a</sup> 1.5 eq of acetic anhdride was used

<sup>b</sup> Yields of isolated products

Scheme 2



solvent-free conditions. Therefore, omitting the solvent makes an easy workup procedure and increases the rate of reaction.

In order to generalize the catalytic efficiency of ZSM-5-SO<sub>3</sub>H for other acylating agents, we tried the acylation of 4-nitrobenzaldehyde with different carboxylic acid anhydrides (Table 4), while most literature methods employ only acetic anhydride for 1,1-diacetate formation. Acylation with butyric, isobutyric, pentanoic, and hexanoic anhydride resulted in good yield of the 1,1-diacylates **2a–2d**.

Then, we investigated the use of ZSM-5-SO<sub>3</sub>H as catalyst in deprotection of acylals to the corresponding aldehydes by treatment of acylals in ethanol at 50 °C. By this procedure several aliphatic, aromatic, and  $\alpha$ , $\beta$ -unsaturated 1,1-diacetates have been transformed into the corresponding aldehydes in high yields (Table 3). It is worth mentioning that aliphatic 1,1-diacetates provided the desired aldehydes within 10 min with much better yield than other reported methods [54, 55]. The interesting feature to note during the deprotection studies was the 1,1-diacetate of aromatic aldehydes needed longer reaction times (30–60 min) than those of aliphatic aldehydes (10 min). This permits the chemoselective deprotection of 1,1-diacetate of an aliphatic aldehyde over an aromatic aldehyde.

A comparative study was done for the use of ZSM-5-SO<sub>3</sub>H with some of the reported catalysts for the synthesis of acylals from 4-methylbenzaldehyde, 4-nitrobenzaldehyde, and furfural with respect to the amounts of acetic anhydride, reaction time, and the yield of the products (Table 5). It is worth mentioning that reactions with the reported catalysts required a larger amount of acetic anhydride, catalyst, and longer reaction time. Reaction with Zeolite-Y as the catalyst was completed after 60-480 min and needed 3 equivalents of acetic anhydride. The formation of an acylal from furfural resulted in failure when AlPW<sub>12</sub>O<sub>40</sub> was used as catalyst. Reaction in the presence of  $H_6P_2W_{18}O_{62}$  needed 10 eq of acetic anhydride. In some methods, the preparation of 1,1-diacetates was performed in solvents such as CH<sub>2</sub>Cl<sub>2</sub>. Most of the catalysts were used only for protection of aldehydes, but

**Table 4** Conversion of 4-nitrobenzaldehyde into 1,1-diacylates with carboxylic acid anhydrides

Entry	Anhydride <sup>a</sup>	Prod.	Time/min	Yield/% <sup>b</sup>
1	(C <sub>3</sub> H <sub>7</sub> CO) <sub>2</sub> O	2a	30	85
2	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CO) <sub>2</sub> O	2b	40	83
3	$(C_4H_9CO)_2O$	2c	25	89
4	$(C_5H_{11}CO)_2O$	2d	20	89

<sup>a</sup> 2.0 eq of anhydrides were used

<sup>b</sup> Yields of isolated products

ZSM-5-SO<sub>3</sub>H can be used for deprotection as well as protection of aldehydes. Also, comparison between ZSM-5-SO<sub>3</sub>H and SSA, a similar sulfonated catalyst, is interesting. The novelties of ZSM-5-SO<sub>3</sub>H over SSA are: (1) SSA was used only for protection of aldehydes, but ZSM-5-SO<sub>3</sub>H can be used for deprotection as well as protection; (2) SSA was used for protection of aldehydes up to 3 mmol, but ZSM-5-SO<sub>3</sub>H can be used for protection of aldehydes up to 25 mmol; (3) ZSM-5-SO<sub>3</sub>H is a reusable catalyst but there is no report about reusability of SSA in protection of aldehydes; (4) SSA shows selectivity in the acylation of aldehydes with different substituents only in CH<sub>2</sub>Cl<sub>2</sub>, whereas we found that ZSM-5-SO<sub>3</sub>H is a selective catalyst in solvent-free conditions as well as in CH<sub>2</sub>Cl<sub>2</sub>; (5) ZSM-5-SO<sub>3</sub>H is a catalyst for acylation of aldehydes with different carboxylic acid anhydrides (Table 4), while the SSA method employs only acetic anhydride; and (6) reaction time and yield are better when ZSM-5-SO<sub>3</sub>H is used as catalyst, especially in the case of heterocyclic and aliphatic aldehydes (Table 5).

The results clearly show that ZSM-5-SO<sub>3</sub>H promotes the reactions more effectively than the other catalysts and should be considered as one of the best choices for selecting an economically convenient, user friendly catalyst.

Finally, we were interested in studying the reusability of the catalysts because of economic and environmental aspects. For this purpose the reaction of 4-methylbenzaldehyde with acetic anhydride was chosen as a model reaction in the presence of ZSM-5-SO<sub>3</sub>H in both heterogeneous and solvent-free conditions. At the end of each run, the catalyst was recovered from the reaction mixture by addition of ethyl acetate in the solvent-free and dichloromethane in heterogeneous reactions, simple filtration and drying at 100 °C, and then reused. The recycled ZSM-5-SO<sub>3</sub>H was used for further runs, and its activity did not show any significant decrease even after four runs. Also, the preparative efficiency of the present method was further established, for example, by scaling up of benzaldehyde to approximately 25-fold, resulting in the respective 1,1-diacetate in nearly quantitative yield under the similar reaction conditions.

In conclusion, ZSM-5-SO<sub>3</sub>H has been found to be a novel, highly efficient, low-cost catalyst for 1,1-diacetate formation from aliphatic and aromatic aldehydes under solvent-free conditions at room temperature. This method is selective for the preparation of 1,1-diacetates from aldehydes in the presence of ketones. 1,1-Diacetates can be conveniently deprotected by using ZSM-5-SO<sub>3</sub>H in ethanol. Operational simplicity without need of any solvent, exceptionally fast, low cost, and non-toxic nature of the catalyst, high yields, excellent chemoselectivity, applicability to large-scale reactions, and reusability of the catalyst

Substrate	Catalyst	Ac <sub>2</sub> O/eq	Time/min	Yield/%	Ref
н <sub>3</sub> с-Сно	P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	2.5	45	87	[16]
	SO4 <sup>2-</sup> /SnO2	2.0	15	97	[32]
	InCl <sub>3</sub>	1.0	60	96	[59]
	$H_6P_2W_{18}O_{62}$	10	30	92	[58]
	SSA	2.0	30	92	[60]
	Zeolite-Y	3.0	180	97	[30]
	ZSM-5-SO <sub>3</sub> H	1.0	1.0	97	This work
О2N-СНО	P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	2.5	45	89	[16]
	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	2.0	50	99	[32]
	InCl <sub>3</sub> <sup>a</sup>	1.0	240	88	[59]
	$AlPW_{12}O_{40}$	1.0	45	89	[57]
	$H_6P_2W_{18}O_{62}$	10	30	88	[58]
	SSA	2.0	15	95	[60]
	Zeolite-Y <sup>b</sup>	3.0	420	98	[30]
	ZSM-5-SO <sub>3</sub> H	1.5	4.0	97	This work
H	P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	2.5	45	83	[16]
	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	2.0	50	99	[32]
	InCl <sub>3</sub>	1.0	30	92	[59]
	AlPW <sub>12</sub> O <sub>40</sub>	1.0	30	0	[57]
	SSA	2.0	25	65	[60]
	Zeolite-Y	3.0	60	90	[30]
	ZSM-5-SO <sub>3</sub> H	1.0	1.0	98	This work

Table 5 Comparison of the effect of catalysts for 1,1-diacetate synthesis from 4-methylbenzaldehyde, 4-nitrobenbenzaldehyde, and furfural

<sup>a</sup>  $CH_2Cl_2$  used as solvent

<sup>b</sup> Reaction was carried out at 70 °C

are the key features of this methodology. Further applications of this catalyst to other transformations are currently under investigation.

# Experimental

All chemicals were purchased from Merck and Fluka chemical companies. The products were characterized by comparing the physical data with those of known samples or by their spectral data. Infrared spectra were recorded on a Nicolet (impact 400D model) FTIR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX 400 Avance spectrometer in CDCl<sub>3</sub> as the solvent and TMS as internal standard. Column chromatography was

performed using silica gel 60 (230-400 mesh). All yields refer to isolated yield.

# Catalyst preparation

The ZSM-5 zeolite samples with Si/Al ratios of 80 were synthesized according to a previously published method [56]. Sodium chloride (2.50 g, 0.04 mol) and 0.59 g of hydrated aluminum sulfate (0.0009 mol) were dissolved in 10.12 cm<sup>3</sup> of distilled water (0.56 mol). Then 1.89 g of tetrapropylammonium bromide (0.0071 mol), 7.12 cm<sup>3</sup> of distilled water (0.39 mol), and 1.09 g of sulfuric acid (0.011 mol) were added. The solution was mixed. Sodium silicate solution (15.0 g, 0.071 mol SiO<sub>2</sub>) was added, and the mixture was stirred vigorously for about 1 h. The pH of

the mixture was 9.15. The mixture was transferred into the autoclave. The autoclave was kept in an oven at 110 °C for about 2 h. Then, the temperature was increased to 230 °C and kept at that level for another 5 h. The solid phase obtained was filtered, washed with distilled water several times, dried at 110 °C for about 12 h, and then calcined at 540 °C for about 6 h.

A 500 cm<sup>3</sup> suction flask was equipped with a constant pressure dropping funnel containing 23.3 g chlorosulfonic acid (0.2 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution, i.e., H<sub>2</sub>O. Then 60.0 g of ZSM-5 was charged into the flask. Chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After the addition was complete, the mixture was shaken for 30 min. ZSM-5-SO<sub>3</sub>H was obtained as a white solid (76 g).

#### General procedure for the synthesis of 1,1-diacetates

(1) In CH<sub>2</sub>Cl<sub>2</sub>: a mixture of aldehyde (1 mmol), freshly distilled acetic anhydride (1.0–1.5 mmol), and catalyst (20 mg) in 3 cm<sup>3</sup> dry dichloromethane was stirred at ambient temperature for appropriate time (as mentioned in Table 3). After completion of the reaction (GC or TLC) the mixture was diluted with 10 cm<sup>3</sup> dichloromethane and filtered to separate the catalyst. The filtrate was washed with water (2 × 10 cm<sup>3</sup>), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuum to give pure 1,1-diacetate or chromatographed on silica gel [petroleum ether (60–80 °C)— ethyl acetate] where necessary.

Acylation with longer chain carboxylic acid anhydrides was also carried out by this procedure, using 2.0 eq of the appropriate anhydrides.

(2) Under solvent-free conditions: to a mixture of aldehyde (1.0 mmol) and catalyst (20 mg) was added acetic anhydride (1.0–1.5 mmol) at room temperature, and the neat reaction mixture was stirred magnetically for an appropriate time (Table 3). The course of the reaction was monitored by TLC and GC. After completion of the reaction, the reaction mixture was diluted with 15 cm<sup>3</sup> ethyl acetate, and the products were isolated as described in procedure (1).

# (4-Nitrophenyl)methylene 1,1'-dibutyrate (**2a**, C<sub>15</sub>H<sub>19</sub>NO<sub>6</sub>)

IR (KBr):  $\bar{\nu} = 3,089$ , 2,961, 1,763, 1,609, 1,524, 1,464, 1,349, 1,169, 978, 854 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.93$  (t, 6H, J = 7.2 Hz), 1.67 (sext, 4H, J = 7.2 Hz), 2.33–2.40 (m, 4H), 7.69 (d, 2H, J = 8.8 Hz), 7.76 (s, 1H), 8.23 (d, 2H, J = 8.4 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 13.4$ , 18.1, 35.8, 88.1, 123.8, 127.8, 142.3, 148.5, 171.2 ppm.

# (4-Nitrophenyl)methylene 1,1'-bis(2-methylpropanoate) (**2b**, C<sub>15</sub>H<sub>19</sub>NO<sub>6</sub>)

IR (KBr):  $\bar{\nu} = 3,089, 2,968, 1,764, 1,609, 1,528, 1,464, 1,350, 1,176, 980, 855 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): <math>\delta = 1.21$  (d, 6H, J = 10.0 Hz), 1.26 (d, 6H, J = 10.0 Hz), 2.62–2.69 (m, 2H), 7.71 (d, 2H, J = 8.8 Hz), 7.76 (s, 1H), 8.29 (d, 2H, J = 8.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 18.5, 18.7, 33.9, 88.2, 123.9, 127.7, 142.4, 148.6, 174.7$  ppm.

# (4-Nitrophenyl)methylene 1,1'-dipentanoate

#### $(2c, C_{17}H_{23}NO_6)$

IR (KBr):  $\bar{\nu} = 2,979, 1,762, 1,610, 1,529, 1,464, 1,350, 1,155, 981, 853 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): <math>\delta = 0.91$  (t, 6H, J = 7.2 Hz), 1.67 (sext, 4H, J = 7.2 Hz), 1.64 (quint, 4H, J = 7.6 Hz), 2.35–2.45 (m, 4H), 7.71 (d, 2H, J = 8.4 Hz), 7.77 (s, 1H), 8.26 (d, 2H, J = 8.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 13.6, 22.1, 26.6, 33.6, 88.2, 123.8, 127.8, 142.3, 148.6, 171.5 ppm.$ 

# (4-Nitrophenyl)methylene 1,1'-dihexanoate (**2d**, C<sub>19</sub>H<sub>27</sub>NO<sub>6</sub>)

IR (KBr):  $\bar{\nu} = 2,958, 1,764, 1,609, 1,529, 1,464, 1,350, 1,166, 986, 853 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): <math>\delta = 0.89$  (t, 6H, J = 7.2 Hz), 1.28–1.38 (m, 8H), 1.67 (quint, 4H, J = 7.2 Hz), 2.38–2.44 (m, 4H), 7.71 (d, 2H, J = 8.6 Hz), 7.78 (s, 1H), 8.28 (d, 2H, J = 8.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 13.9, 22.2, 24.3, 31.1, 33.9, 86.2, 123.8, 127.8, 142.3, 148.6, 171.5 ppm.$ 

# *General procedure for the deprotection of 1,1-diacetates*

A mixture of 1,1-diacetate (2 mmol) and ZSM-5-SO<sub>3</sub>H (20 mg) in 5 cm<sup>3</sup> ethanol was stirred vigorously at 50 °C for a specified time as required to complete the reaction (Table 3). The reaction was monitored by TLC and GC. After completion of the reaction, the reaction mixture was diluted with 20 cm<sup>3</sup> Et<sub>2</sub>O and filtered to separate the catalyst. The filtrate was washed with 20 cm<sup>3</sup> water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure, and the resultant product was passed through a short column of silica gel to afford pure aldehyde.

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