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Sulphated zirconia catalyzed acylation of phenols, alcohols and amines under solvent free conditions

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Abstract

Sulphated zirconia prepared by the treatment of a high surface area zirconia (320 $m^2\ g^{-1}$) with 1 N H_2SO_4 shows a strong acidity after calcination at 893 K. It is comparable to that of zeolites, with an enthalpy of adsorption of NH_3 close to 130 kJ mol^{-1}. The isotherm of N_2 adsorption at 77 K on the sulphated zirconia shows characteristic of mesoporous solid having surface area about 125 $m^2\ g^{-1}$, and pores of 4 nm as determined applying the BJH method. The sulphated zirconia obtained by sulphation has 14.5 wt.% S just after oven drying and 1.8 wt.% S after calcination at 893 K. The X-ray diffraction pattern of the calcined sample shows the presence of an intensive peak at $2\theta = 30$ characteristic of the tetragonal structure. This solid acid has been applied to the acylation of a variety of phenols, alcohols and amines with acetic anhydride as an acylating agent under solvent free conditions. The yields reach about 95% in 10 min, and the catalyst can be recycled several times, so that this process could find useful applications.

Keywords: Acylation; Acetic anhydride; Sulphated zirconia; Microcalorimeter

1. Introduction

The acylation of alcohols, phenols and amines is one the most frequently used transformations in organic synthesis. Organic esters represent an important family of intermediates widely employed in the synthesis of fine chemicals, drugs, plasticizers, perfumes, food preservatives, pharmaceuticals and chiral auxillaries [1,2]. Acylation of alcohols with acid anhydrides is usually performed in the presence of stoichiometric amounts of bases such as tertiary amines [3,4], tributyl phosphine [5], 4-dimethylamino pyridine [6] and 4-pyrrolidino pyridine [7]. On the other hand protic acids, such as *p*-toluenesulphonic acid [8], Lewis acids such as metal chlorides [9–12], metal perchlorates [13–15], yttria–zirconia-based catalysts [16], metal–salen complexes [17], metal oxides such as ZnO [18], montmorillonites [19–21], perchloric acid adsorbed on silica gel [22], silica sulphuric acid [23], aluminium decatungstophosphate [24], zeolites [25], Nafion-H [26], KF-Al_2O_3 [27], $ZrOCl_2{\cdot}8H_2O$ [28], silica embedded–triflate catalysts [29], manganese(III) acetylacetonato complexes [30], indium trihalides [31] and bis(cyclopentadienyl)zirconium dichloride [32] have also been utilized to achieve the acylation of alcohols, phenols, thiols, and amines. Some of the above described protocols use harsh reaction conditions, use of hazardous materials, use of excess acylating agent, scope for potential side reactions with acid-sensitive substrates and in most of the cases being applicable to alcohols only. For instance, pyridine derivatives, such as DMAP and 4-pyrrolidinopyridine are highly toxic, Bu_3P is flammable and air sensitive, metal triflates lead to potential side reactions (rearrangement, dehydration, etc.) with acid-sensitive substrates necessitating the use of a large excess of AC_2O and low temperature, in addition to the use of a costly catalyst. Recently $ZrCl_4$ and $ZrOCl_2$ have been utilized to achieve the acylation but these are highly corrosive, hygroscopic and difficult in handling.

Less expensive Zr(IV) compounds exist such as sulphated zirconia, a stable non-hazardous compound and ideal catalyst

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for catalytic applications. Sulphated zirconia (SZ) has been shown to be active for isomerization [33,34], cracking [35], alkylation of olefins [36,37], Friedel–Crafts acylation [38–44], tetrahydropyranylation of alcohols and phenols, synthesis of 1,5-benzodiazepines, *C*-alkylations [45]. Surprisingly the *O* or *N*-alkylation by acids has not been investigated and this work deals with the preparation of sulphated zirconia, which is active towards the *O* or *N*-acylation of alcohols, phenols and amines with acid anhydride as an acylating agent under solvent free conditions.

2. Experimental

2.1. Catalyst preparation

The catalyst was synthesized by the following procedure. Zirconium hydroxide was precipitated from $ZrOCl_2$ (Loba, L.R. grade) at constant pH 10 with the help of NH_4OH. The precipitate was aged at 353 K for 12 h, filtered and washed several times until free from chloride ions and dried at 393 K for 24 h. To prepare sulphated ZrO_2, a 1.0 M sulphuric acid solution (350 ml) was poured into the finely powdered $Zr(OH)_4$ (35 g), stirred for 4 h, filtered and dried at 393 K for 12 h and calcined at 893 K for 4 h.

The acid properties were determined by adsorption of ammonia at 353 K, using a Tian–Calvet microcalorimeter coupled to a volumetric ramp [46]. The solids were first pre-treated in vacuum at 723 K for 3 h, then small increments of NH_3 were introduced in the cell, the heat of interaction was measured by calorimetry, and the isotherm determined by volumetry. The differential enthalpy of adsorption is a measure of the acid strength of the sites, and the amount of NH_3 adsorbed gives their number.

2.2. General experimental procedure

All substrates are commercially available and used without further purification. In a typical procedure, 2-naphthol (360 mg, 2.5 mmol) was reacted with acetic anhydride (0.24 ml, 2.5 mmol) in the presence of sulphated zirconia catalyst (50 mg) for the required period of time at room temperature under stirring. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was treated with saturated bicarbonate solution and the product was extracted into ethyl acetate. The solvent was removed under vacuum to afford 2-naphthyl acetate as pure product (445 mg, 98% yield). The isolated yields are calculated on the basis of the weight of the pure product obtained. In all the reactions only the corresponding product was obtained without any by-product.

The products are characterized on the basis of ^{1}H NMR and GC–MS. Analytical data of representative compounds are shown below:

- β-Naphthyl acetate ($C_{12}H_{10}O_2$) (entry 1). Yield: 97%; brown solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.8 (3H, m, ArH), 7.56 (1H, s, ArH), 7.47 (2H, m, ArH), 7.24 (1H, d, J = 8.62 Hz, ArH), 2.36 (3H, s, COCH3); GC–MS: *m/z* (%) 186 (*M* +20), 144 (1 0 0), 115 (45).
- 4-Bromo-phenyl acetate ($C_8H_7BrO_2$) (entry 2). Yield: 98%; colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (2H, d, J = 8.5 Hz, ArH), 6.97 (2H, d, J = 8.5 Hz, ArH), 2.28 (s, 3H, $COCH_3$); GC–MS: *m/z* (%) 215 (*M* +22), 172 (1 0 0), 92 (31), 64 (31), 43 (50).
- 4-Acetyl-phenyl acetate ($C_{10}H_{10}O_4$) (entry 3). Yield: 90%; colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (2H, d, J = 8.8 Hz), 7.16 (2H, d, J = 8.8 Hz), 2.29 (3H, s, $COCH_3$); GC–MS: *m/z* (%) 178 (*M*+ 42), 136 (1 0 0), 120 (99), 93 (31), 43 (49).
- Phenyl acetate ($C_8H_8O_2$) (entry 4). Yield: 94%; colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (2H, t, ArH), 7.27 (1H, t, ArH), 7.12 (2H, d, J = 7.36 Hz, ArH), 2.32 (3H, s, $COCH_3$); GC–MS: *m/z* (%) 136 (*M*+ 10), 94 (1 0 0), 43 (24).
- Benzyl acetate ($C_8H_{10}O_2$) (entry 5). Yield: 93; colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (5H, m, ArH), 5.08 (2H, s, $PhCH_2$), 2.06 (3H, s, $COCH_3$); GC–MS: *m/z* (%) 150 (*M* +34), 108 (1 0 0), 91 (16), 43 (1 0 0).
- Cyclopentyl acetate ($C_7H_{12}O_2$) (entry 6). Yield: 90%; colorless liquid; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.15 (1H, m, OCH), 2.01 (3H, s, $COCH_3$), 1.9 (2H, t, CH_2), 1.8 (2H, t, CH_2), 1.7 (2H, m, CH2), 0.1 (2H, m, CH_2); GC–MS: *m/z* (%) 128 (*M*+ 2), 112 (34), 97 (14), 87 (99), 55 (55), 43 (1 0 0).
- 1-Methyl-hexylacetate ($C_{10}H_{20}O_2$) (entry 7). Yield: 85%; colorless liquid; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.85 (1H, m, OCH), 2.01 (3H, s, $COCH_3$), 1.6 (2H, d, CH_2), 1.5 (2H, m, CH_2), 1.4 (2H, m, CH_2), 1.3 (3H, s, CH_3), 1.2 (2H, m, CH_2), 1.18 (2H, m, CH_2), 0.9 (3H, t, CH_2CH_3); GC–MS: *m/z* (%) 172 (*M*+), 136 (32), 120 (1 0 0), 43 (42).
- *N*-Phenylacetamide (C_8H_9NO) (entry 8). Yield: 93%; white solid; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.79 (1H, s, brs, PhNH), 7.49 (2H, d, ArH), 7.30 (2H, t, ArH), 7.10 (1H, t, ArH), 2.05 (3H, s, $COCH_3$); GC–MS: *m/z* (%) 135 (*M*+ 22), 94 (7), 93 (1 0 0), 66 (11), 43 (19).
- *N*-Benzylacetamide ($C_9H_{11}NO$) (entry 9). Yield: 85%; white solid; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.47–7.04 (5H, m, ArH), 6.4 (1H, s, brs, $ArCH_2NH$), 4.35 (2H, d, $PhCH_2$), 1.94 (3H, s, $COCH_3$); GC–MS: *m/z* (%) 150 (*M*+ 14), 149 (80), 106 (1 0 0), 91 (40), 79 (24), 43 (31).
- 4-Acetylmorpholine ($C_6H_{11}NO_3$) (entry 10). Yield: 94%; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.66 (2H, t, OCH_2), 3.59 (2H, t, NCH_2), 3.47 (2H, t, NCH_2), 2.09 (3H, s, $COCH_3$); GC–MS: *m/z* (%) 129 (*M* +39), 114 (20), 86 (45), 57 (1 0 0), 56 (55.8), 43 (82), 42 (18), 29 (20), 15 (16).

2.3. Results and discussion

The initial hydrated zirconia shows a surface area of about 320 $m^2\,g^{-1}$, reduced to <70 $m^2\,g^{-1}$ upon calcination at 823 K and 40 $m^2\,g^{-1}$ at 923 K [47]. The sulfated zirconia, obtained by sulphation of this hydrated zirconia contains about 14.5 wt.% S just after oven drying, and 1.8 wt.% S after calcination at 893 K. The X-ray diffraction pattern of the calcined sample (Fig. 1) shows the presence of an intense peak at $2\theta = 30$ characteristic of the tetragonal structure, and the absence of any peak at $2\theta = 28.2$

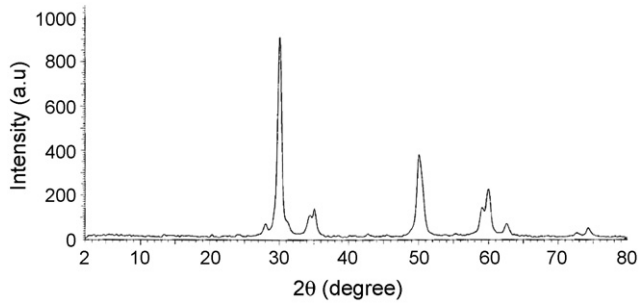


Fig. 1. X-ray diffraction pattern of the sulphated zirconia used as catalyst.

characteristic of a monoclinic structure. It is clearly shown in the literature that the sulphated zirconia calcined above 800 K has tetragonal structure due to the interaction of sulphate groups with the surface of zirconia [48,49].

The isotherm of N_2 adsorption at 77 K on the sulphated zirconia is shown in Fig. 2. This isotherm is characteristic of a mesoporous solid. The solid has a surface area of about 125 $m^2\,g^{-1}$, and pores of 4 nm (Fig. 3), as determined by the BJH method, this is favorable for a fast diffusion of reactants.

The distribution of acid strengths of the solid is reported in Fig. 4. The solid contains about 0.4 mequiv. g^{-1} with strength comparable to that of zeolites. The surface properties of this solid are very close to those of the conventional sulphated zirconia sample reported by Quaschning et al. [50]. Non-sulfated zirconia shows only a very weak [51].

The results of the acylation of phenols, alcohols and amines using sulphated zirconia (Scheme 1) are shown in Table 1, which amply demonstrates the generality and scope of the reaction with regard to structurally diverse phenols, alcohols and amines. Thus, the reaction of the substrate with acetic anhydride in presence of 50 mg of catalyst (representing 0.02 mequiv. of acid sites, therefore a "catalytic amount") under solvent free conditions at room temperature provided the corresponding acetate in excellent yields (85–98%). The reaction is also studied without the

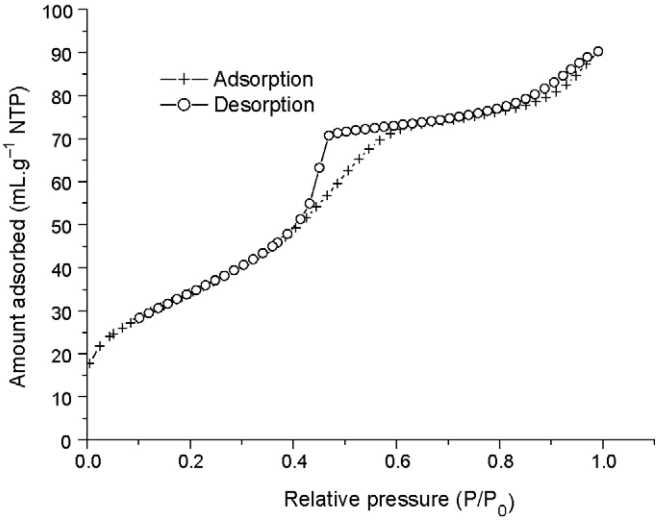


Fig. 2. Isotherm of nitrogen adsorption on the solid acid catalyst at 77 K.

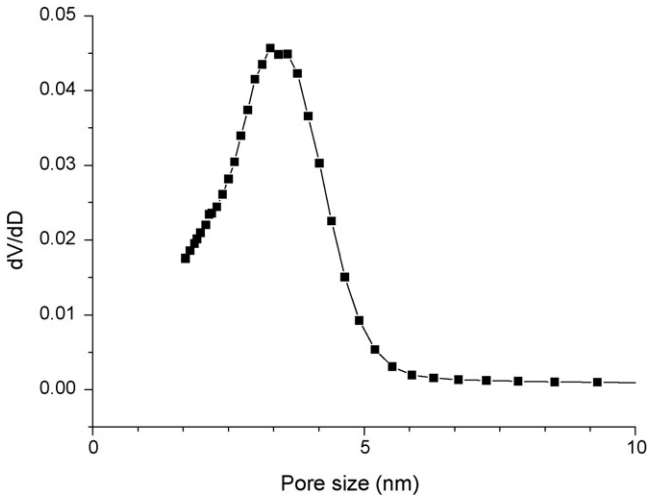


Fig. 3. Distribution of pore sizes computed by BJH theory.

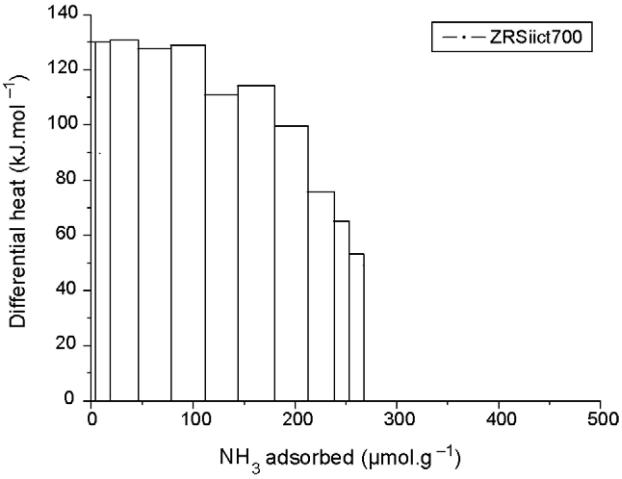
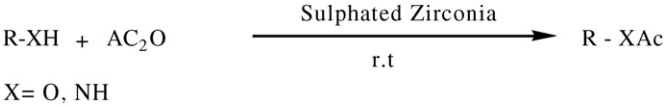


Fig. 4. Differential heat of adsorption of ammonia as a function of the amount adsorbed, for sulphated zirconia calcined at 973 K and desorbed at 673 K.

catalyst and with zirconia (before sulphonation) and the results are shown in Table 1 (entry 2).

After completion of the reaction, ethyl acetate is added to the reaction mixture and the catalyst is filtered. The catalyst is oven dried and reused for four cycles with consistent activity (Table 1, entry 2).

The described methodology illustrates a very simple acylation procedure, with wide applicability, extending the scope to benzylic, primary, secondary, tertiary, cyclic alcohols. Sterically hindered and electron deficient phenols and amines are efficiently acylated under similar conditions and solvent free conditions.

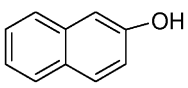
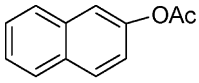
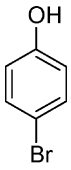
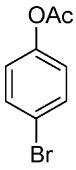
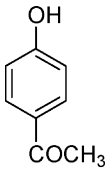
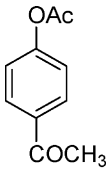
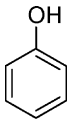
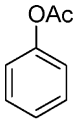
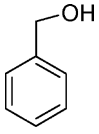
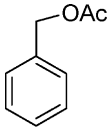
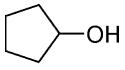
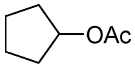
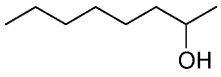
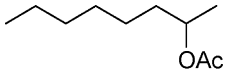
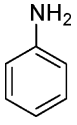
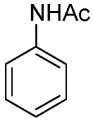
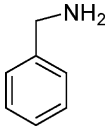
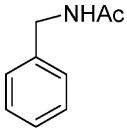
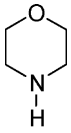
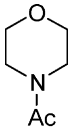


X= O, NH

R= 2-naphthyl, p-bromophenyl, p-acylphenyl, phenyl benzyl, cyclopentane

Scheme 1.

Table 1
Sulphated zirconia catalyzed acetylation of alcohols, phenols and amines using acetic anhydride as an acetylating reagent[a]

Entry	Substrate	Time (min)	Product	Yield (%)[b]
1		10		97
2		10		98, 97[c], 14[d], 28[e]
3		15		90
4		10		94
5		10		93
6		10		90
7		10		85
8		10		93
9		10		85
10		15		94

[a] Reaction conditions: substrate (2.5 mmol), acetic anhydride (2.5 mmol), catalyst (50 mg), RT.
[b] Isolated yield on the basis of the weight of the pure product obtained.
[c] Isolated yield after fourth recycle.
[d] Yield in blank reaction.
[e] Yield with support (ZrO_2).

3. Conclusions

In conclusion, we have described a mild and efficient acylation procedure for various alcohols, phenols and amines using acetic anhydride as acylating agent in the presence of catalytic amount of sulphated zirconia.

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