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Synthesis of Phenyl Esters Using SiO_2–SO_3H Catalyst in Conventional Heating and Microwave-Irradiated Esterification Processes

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A SiO_2–SO_3H amorphous catalyst containing a small surface area of 115.0 m^2g^{-1} and 1.32 mmol H^+/g was prepared from fine construction sand and sodium carbonate and sulfonated with H_2SO_4. In a 10% (w/w) basis, it is very efficient for catalyzing the esterification of carboxylic acids with phenol. The reaction processes were performed using conventional heating and under microwave irradiation. The yields were higher in the microwave-irradiated esterification. The catalyst could be used for three esterification sequences in both processes.

Keywords: Micro-Meso-Macroporosity Catalyst, Phenyl Esters, Solvent Free Esterification, Microwave Irradiation, Phenyl Acetate, Diphenyl Oxalate, Diphenyl Carbonate Precursor.

1. INTRODUCTION

Silica can be functionalized with sulfonic acid groups in various ways, the simplest method being the direct mixture of silica and sulfuric acid with a mortar and a pestle; such mixture was used by Chavez et al. to catalyze the protection and deprotection of alcohols.[1] More elaborated methods have since being reported, including the reaction of silica with chlorosulfonic acid. The sulfonated silicas have been used as environmentally friendly, reactive, substitutes for sulfuric or toluenesulfonic acid catalysts, including esterification reactions,[2] as recently reviewed by Zolfigol.[3(a, b)]

During our previous studies of reactions promoted by microwave irradiation,[4] we found that metallic Lewis acids such as $ZnCl_2$ or $FeSO_4$, when supported on silica, were excellent catalysts for otherwise difficult-to-promote esterification reactions. However, those catalysts were not able to catalyze esterification reactions of aromatic alcohols, such as benzyl alcohol. We have since then developed an efficient heterogeneous mesoporous silica catalyst, SiO_2–SO_3H, made from construction sand and sulfonated with sulphuric acid, whose characteristics, besides its acidic properties, included small surface area (115 m^2g^{-1}), and a high thermal stability for catalytic applications. The SiO_2–SO_3H was shown to be a very powerful catalyst for the direct production of benzyl benzoate from benzyl alcohol and benzoic acid using microwave irradiation,[5] which prompted us to apply that process to the formation of phenol esters as well. It is important to emphasise that, when esterification is performed using mineral acid catalysts (concentrated H_2SO_4,[6] H_3PO_4,[7] HCl[8]), an excess of the alcohol must be used because of the reversibility of the reaction, and an organic solvent must be used to remove the water formed. These facts lead to environmental problems because of the mineral acid and the organic solvent that must be removed during the workup.

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The processes of esterification using the modified silica can be accomplished without solvent, and they are irreversible, for the silanol groups present in the solid catalyst adsorb the water by-product. The unnecessary use of different organic solvents, and the abolishment of the use of excesses of acid or alcohol are the added bonuses from this reaction irreversibility.

In this present study we produced the phenol esters of the aliphatic acids, formic and acetic, the aromatic acids, nicotinic and salicylic, as well as the diester of oxalic acid, and a few remarks about the importance of those esters must be made. For instance, the acetylation of alcohols, i.e., the formation of acetates, is a major synthetic procedure for the protection of alcohols and phenols, but acetic acid, as we use here, is rarely the acyl donor, the reactions requiring acetic anhydride or acyl chloride.[9] Due to its importance, a large number of different acetylation methods are available,[9,10] but the vast majority suffers from side products, harsh reaction conditions, the use of air-sensitive or toxic promoters, and reaction times of the order of days;[9] moreover, alcohols which are poor nucleophiles, such as phenol, besides requiring prolonged acetylation reaction times, they also need anhydride activators.[11] Phenyl acetate have also been successfully employed as a general reagent for highly selective N-acetylation of primary amino groups in the presence of other alcohol and secondary amino groups within the acetylated molecules.[12]

The aromatic acids chosen for this work were the nicotinic (niacin) and salicylic one's for the production of phenyl nicotinate and the phenyl salicylate (salol), respectively.[13–15] We further tested SiO_2–SO_3H with phenol for the production of the di-ester of oxalic acid, which may be of interest in organic synthesis for alkylation reactions.[16] Recently it was reported the synthesis of $(PhOCO)_2$ by transesterification of the dimethyl[17] or of the diethyl[18] esters of oxalic acid with phenol, using transition metal oxide catalysts supported on silica. In those works, the authors applied that precursor for the synthesis of diphenyl carbonate, which can itself be used in transesterification reactions with bisphenol-A, for the production of the very important phenyl polycarbonates that usually require the employment of the extremely poisonous phosgene, $COCl_2$, in their preparation.

2. EXPERIMENTAL DETAILS

2.1. Raw Materials and Chemicals

Sand was available from wholesales. Carboxylic acids (formic, acetic, benzoic, nicotinic, salicylic), phenol, sodium carbonate and concentrated sulfuric acid, all from VETEC, were used without previous purification.

2.2. Instrumentation

The characterization of the precursor silica gel[5(a)] and catalyst[5(b)] by IR, SEM, EDS, XRD, DTA and N_2 adsorption–desorption have been discussed previously. Ester contents and yields of reaction products were determined with a Shimadzu GC/MS-QP 2010 Gas Chromatograph/Mass Spectrometer equipped with a 30 m Agilent J&W GC DB-5 MS column and an AOC 5000 AUTO INJECTOR. Direct insertion spectra were measured at 70 eV. Quantitative analyses were performed on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector (FID). The initial temperature was 60 °C for 2 min, the temperature was increased to 220 °C at 10 °C min^{-1}, and finally, to 240 °C at 5 °C min^{-1}, where it was held for 7 min. The injector and detector temperatures were kept at 250 °C. A Bruker micrOTOF Q II-ESI-TOF Mass Spectrometer was used in positive mode detection, with an internal calibration solution containing 10 mg/mL of Na-TFA (TOF). Analytical conditions: End Plate: 500 Volts; Capillary: 4500 Volts; Capillary Exit: 120 Volts; Skimmer 1: 50 Volts; Skimmer 2: 22 Volts; Transfer: 57 μs; Dry Gas Temp: 180 °C; Dry Gas Flow: 4 L/min; Neb Gas Pressure of nitrogen gas: 0.4 Bar. ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 400 spectrometer using $CDCl_3$ (Aldrich) as solvent and TMS as internal reference. Melting points (uncorrected) were determined on a Koffler hot plate. All reactions were carried out under atmosphere pressure, using microwave irradiation or a heating mantle and monitored by TLC with pre-prepared plates (Silica Gel 60 F254 on aluminum). The chromatograms were visualized by the use of UV or an ethanolic vanillin developing agent. Merck silica gel (230–400 mesh) was used for purification of products by flash column chromatography using *n*-hexane and ethyl acetate (8:2) as eluents.

2.3. Preparation of the Silica Gel and the Sulfonated Silica (SiO_2–SO_3H)

Construction sand, sifted through a 230 mesh sieve (100.0 g) and 200.0 g of sodium carbonate were homogenized and transferred to porcelain crucibles, which were heated at 850 °C for 4 h. The hot solid mixture was transferred to a fritted glass filter and washed with 200–300 mL of boiling water. The filtered solution was acidified to pH 1 with hydrochloric acid, and the white precipitate was filtered under reduced pressure and dried at 400 °C for 4 h. The resulting silica was passed through a 24 mesh sieve for standardization. A 10.0 g portion of the silica gel was mixed with 20.0 mL of concentrated H_2SO_4. The mixture was stirred for 12 h at room temperature, filtered under reduced pressure, kept in an oven at 150 °C for 4 h, cooled to room temperature and stored in a desiccator. The acid strength of the catalyst was measured by potentiometric titration using standard NaOH, and the amount of H^+ in SiO_2–SO_3H was found to be 1.32 mmol of H^+ per gram.

2.4. Typical Procedures: Synthesis of Phenyl Esters

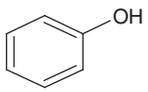
In all reactions involving SiO_2–SO_3H, the amounts of carboxylic acid (1.0 mmol) and phenol (0.0941 g, 1.00 mmol)

were uniform. The amount of catalyst in each run was adjusted to maintain a constant (10%) mass-to-mass ratio to the phenol. All reactions were heated with a heating mantle (5 h, the final temperature of the slurries did not exceed 120 °C) or by irradiation (5 or 9 min) in an unmodified MW oven (900 GHz)/360 W using an unstoppered 125-mL two-necked round bottom flask.[2] The final temperature of the slurries did not exceed 73 °C.

2.5. Reaction Using Heating Mantle

To a two-necked round bottom flask containing SiO_2–SO_3H (10% w/w) was added the carboxylic acid (1.00 mmol) and phenol (1.00 mmol). The reaction mixture was heated in a heating mantle at temperatures ranging from 90 to 120 °C for 5 h, the reaction being accompanied by TLC. The vessel was cooled to room temperature, 30 mL of diethyl ether was added, and the mixture was filtered. The organic extract was washed with 10.0 mL of saturated $NaHCO_3$, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a chromatographic column using hexane and ethyl acetate as eluent to obtain the pure phenyl esters as colorless oil or a white solid (diester of oxalic acid) in excellent yields (CG/MS, Table I).

Table I. Esterification reaction from carboxylic acids with phenol.



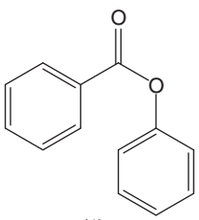
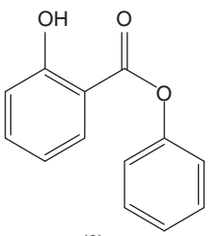
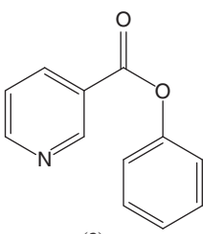
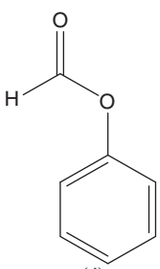
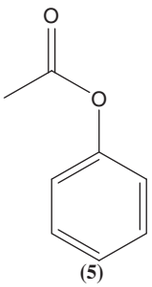
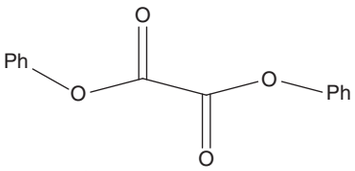
Phenyl esthers	*Y* (%) MW	*Y* (%) Heating mantle	Time
 **(1)**	96.45	94.23	MW 9.0 min HM 5 h
 **(2)**	85.11	80.21	MW 9.0 min HM 5 h
 **(3)**	63.46	60.34	MW 5.0 min HM 5 h
 **(4)**	–	80.05	HM 5 h

Table I. Continued.

Phenyl esthers	*Y* (%) MW	*Y* (%) Heating mantle	Time
 (5)	–	77.10	HM 5 h
 (6)	74.19	69.65	MW 5 min HM 5 h

Notes: Reaction conditions: Carboxylic acid, 1.00 mmol; phenol, 1.00 mmol; reaction of oxalic acid (1.00 mmol) with phenol (2.00 mmol), 14% or 20% (w/w) SiO_2–SO_3H, MW 360 W at approximately 70 °C. Reactions involving formic acid or acetic acid with phenol were realized using heating mantle. Products were purified by column chromatography using neutral SiO_2 as the stationary phase with hexane/ethyl acetate (8:2) as eluent.

The filtered catalyst was washed with 10 mL of diethyl ether and dried at 150 °C for 2 h before re-use. Esters were identified by GC/MS, ^{1}H NMR and ^{13}C NMR.

2.5.1. Microwave Irradiation

A mixture of aromatic carboxylic acid or oxalic acid (1.00 mmol), phenol (1.00 mmol) and SiO_2–SO_3H (0.110 g, 10% w/w phenol) was irradiated in a microwave oven. After 9 min (5 min for oxalic acid) of irradiation, the temperature of the reaction rose to 70 °C. The vessel was cooled to room temperature, 30 mL of diethyl ether was added, and the mixture was filtered. The workup was identical to that described above.

2.5.2. Characterization Data

Phenyl Benzoate.[19] White solid; mp. 68–70 °C. MS *m/z* 198 (4.10) $[M]^+$ $C_{13}H_{10}O_2^+$, 105 (100.00) $[M\text{-}C_6H_5O]^+$ $C_7H_5O^+$, 77 (36.20) $[M\text{-}C_7H_5O_2]^+$ $C_6H_5^+$. IR (KBr) υ_{max} 3072, 3058, 3043, 2967, 2924, 2870, 2866, 1729, 1596, 1591, 1586, 1487, 1458, 1377, 1311, 1296, 1262, 1199, 1177, 1167, 1158, 1153, 1081, 1069, 1026, 1001, 922, 916, 752, 704, 697, 662 and 606 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 8.23 (o-acid), 7.63 (p-acid), 7.56 (o-phenyl), 7.48 (m-phenyl), 7.28 (p-phenyl), 7.27 (m, acid) ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 165.2 (carbonyl), 150.62 (quaternary, phenyl), 133.69 (m-acid), 130.18 (o-acid; quaternary, acid), 129.51 (m-phenyl), 128.58 (m-acid), 125.9 (p-phenyl), 121.73 (o-phenyl).

Phenyl Salicylate.[20(a, b)] White solid; mp. 41–43 °C (lit. 41.5 °C). MS *m/z* 214 (07.68) $[M]^+$ $C_{13}H_{10}O_3^+$, 121 (100.0) $[M\text{-}C_6H_5O]^+$ $C_7H_5O_2^+$. IR (KBr) υ_{max} 3237, 3073, 3047, 1696, 1616, 1600, 1592, 1584, 1509, 1495, 1488, 1457, 1399, 1333, 1301, 1250, 1229, 1208, 1193, 1163, 1167, 1129, 1058, and 1033 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 10.52 (OH), 8.06 (o-salicilate), 7.50 (p-salicilate), 7.43 (m-phenyl), 7.28 (p-phenyl), 7.19 (o-phenyl), 6.94 (m-salicilate). ^{13}C NMR (100 MHz, ppm) 169.02 (carbonyl), 162.28 (C–OH), 150.16 (quaternary phenyl), 136.56 (p-salicilate), 130.43 (o-salicilate), 129.71 (m-phenyl), 126.47 (p-phenyl), 121.73 (o-phenyl), 119.55 (m-salicilate), 117.90 (m-phenyl).

Phenyl Nicotinate.[21] White solid; m.p. 70–72 °C (lit. 70–72 °C). GC: tR = 36.92 min. White solid; mp. 70–74 °C. MS *m/z* 199 (10.20) $[M]^+$ $C_{12}H_9NO_2^+$, 106 (100.00) $[M\text{-}C_6H_5O]^+$ $C_6H_4ON^+$, 78 (88.50) $[M\text{-}C_7H_5O_2]^+$ $C_5H_4N^+$. IR (KBr) υ_{max} 3043, 2955, 2925, 2854, 1740, 1595, 1589, 1574, 1491, 1455, 1450, 1430, 1377, 1328, 1277, 1247, 1200, 1189, 1166, 1124, 1117, 1088, 1073, 1023, 998, 855, 764, 733, 722, 709, 701, 692 and 606 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 9.40 (C(O)–CH–N), 8.59 (CH–N), 8.45 (CH–C(O)), 7.48 (m-py), 7.43 (m-phenyl), 7.30 (p-phenyl), 7.23 (o-phenyl). ^{13}C NMR (100 MHz, ppm) 163.92 (carbonyl), 154.01 (CH–N), 151.39 (C(O)–CH–N), 150.54 (quaternary, phenyl), 137.64 (CH–C–C(O)), 129.64 (m-phenyl), 126.28 (p-phenyl), 125.62 (m-nicotinate), 121.57 (o-phenyl).

Phenyl formate.[21] MS *m/z* 122 (24.88) $[M]^+$ $C_7H_6O_2^+$, 94 (100.00) $[M\text{-}CO]^+$ $C_6H_6O^+$. IR (KBr) υ_{max} 3088, 3065, 3033, 2954, 1875, 1764, 1585, 1496, 1266, 1169, 1032, and 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, 400 MHz), 9.58 (aldehyde), 7.47 (m-aromatic), 7.27 (p-aromatic), 7.26 (o-aromatic). ^{13}C NMR (ppm, 100 MHz) 160.58 (carbonyl), 158.17 (quaternary), 129.63 (m-phenyl), 123.59 (p-phenyl), 116.59 (o-phenyl).

Phenyl Acetate.[22(a, b)] MS m/z 136 (18.00) $[M]^+$ $C_8H_8O_2^+$, 94 (100.00) $[M\text{-}C_2H_2O]^+$ $C_6H_6O^+$. IR (KBr) υ_{max} 3068, 3044, 3034, 2943, 1765, 1694, 1493, 1484, 1456, 1433, 1371, 1291, 1194, 1163, 1070, 1046, 1027 and 1014 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm), 7.43 (m-phenyl), 7.28 (p-phenyl), 7.17 (o-phenyl), 2.31 (methyl). ^{13}C NMR (100 MHz) 169.70 (carbonyl), 150.80 (quaternary), 129.50 (m-phenyl), 125.92 (p-phenyl), 121.70 (o-phenyl), 21.06 (methyl).

Diphenyl Oxalate.[23] White solid; m.p. 136–138 °C (lit. 136 °C). MS m/z 242 (15.91) $[M]^+$ $C_{14}H_{10}O_4^+$, 77 (100.0) $[M\text{-}C_7H_5O_4]^+$ $C_6H_5^+$. IR (KBr) υ_{max} 3043, 2954, 2924, 2866, 1776, 1699, 1586, 1487, 1456, 1378, 1366, 1317, 1304, 1290, 1276, 1255, 1201, 1188, 1181, 1165, 1145, 1070, 1019, 1007, 936, 926, 846, 751, 745, 723, 695 and 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm), 7.43 (m-phenyl), 7.32 (o-phenyl), 7.28 (p-phenyl); ^{13}C NMR (100 MHz), 154.96 (carbonyl), 150.32 (quaternary), 129.63 (m-phenyl), 126.61 (o-phenyl), 121.59 (p-phenyl).

3. DISCUSSION SECTION

One of the interests of our research group is in the development of new substrates for heterogeneous catalysis,[4, 5(a, b)] and our attention was attracted to a silica support that could be made directly from inexpensive construction sand. To access the potential of that support, the silica (surface area 507.00 m^2g^{-1}) was impregnated with concentrated sulfuric acid and after that the mixture was kept under stirring for 12 h at room temperature. Washing and drying resulted in a material, SiO_2–SO_3H, with a surface area 115.00 m^2g^{-1}, that could catalyze the esterification of carboxylic acids with phenol, with excellent yields.

3.1. Esterification Reactions

The main challenge involved in the direct esterification reaction between a carboxylic acid and phenol is the production of water, which has to be removed by adsorption on the silanol groups to impede the reversibility of the reaction. The yields of esters obtained using microwave radiation were higher than those obtained by heating under reflux with a heating mantle, probably because of the increased rotational modes of the polar reagents carboxylic acids and phenol caused by the microwaves irradiation. This increase in vibration must enhances the ease of flow of the reactants through the pores of the catalyst, reducing the reaction times and, consequently, improving the performance of all reaction processes (Table I). In the microwave-irradiated processes, the temperatures of the reaction media did not exceed 75 °C, unlike processes with heating in a thermal blanket, where temperatures reached 120 °C.

Under conventional reaction conditions, i.e., dispersion of the reagents by a suitable solvent and conventional heating, the longer times required to esterify a hydroxyl group directly bound to an aromatic ring can be straightforwardly related to the greater basicity of that hydroxyl, since the resulting negative charge of the anion is stabilized within the aromatic ring. The consequence is the lowering of the nucleophilic strength of that –OH group, which will have difficulty in attacking the partner of the reaction, which is the activated form of the acid. These effects should lead to very poor yields, if one assumes that the esterification reaction under those conditions follows the Fischer esterification mechanism, and this is the main reason why industrial processes rely in acid chlorides or activated anhydrides for the preparation of phenyl esters. In the present synthesis of the esters, the phenyl benzoate was formed in the highest yield using a reaction time of nine minutes, under microwave irradiation and without solvents, followed by the rather good yields of phenyl salicylate and phenyl nicotinate, prepared under the same circumstances. It is possible that the presence of extra functional groups in the molecules of the latter reagents increase their affinity for the Bronsted catalyst surface, hence lowering their overall reactivity towards esterification by phenol molecules. In fact, this behavior of the catalyst could be an indication that under the present circumstances, the Fischer mechanism may still be in operation, the microwaves helping phenol to attack the organic acids which have been highly activated by the combination of MW irradiation and strong Bronsted SiO_2–SO_3H catalyst surface.

The time under ordinary reflux necessary to obtain high yields of the phenyl formate and phenyl acetate was 5 h, which is still a reasonably short time if considering the participation of the acids as reagents. These reactions were not tested in our unmodified MW oven. The formation of by-products was not detected in any of the esterification reactions with phenol.

4. SUPPLEMENTARY MATERIAL

^1H and ^{13}C NMR spectra are presented as supplementary material, and CG/MS for selected synthesis are also included.

5. CONCLUSION

A solid Bronsted acid catalyst, obtained by treating silica gel produced from sand with concentrated sulfuric acid, was employed for the esterification of phenol with aromatic and short chain aliphatic acids. Yields of over 96% phenyl benzoate were obtained with this catalyst using microwave irradiation, and the catalyst could be reused three times before deactivation. The presence of extra functional groups in the acids i.e., pyridine in nicotinic acid, or hydroxyl in salicylic acid, decreases the activity without affecting the catalytic formation of the respective phenyl esters. The high polarity of the reactants and the strong Bronsted character of the catalyst lead to a

high reagent-catalyst affinity, and this affinity appears to increase when the reaction medium suffers the effect of microwave radiation, resulting in good to excellent yields of the esterification processes of the otherwise unreactive phenol alcohol. The diphenyl ester of oxalic acid, the important intermediate for the production of diphenyl carbonate, was obtained directly with this catalyst using phenol and oxalic acid, under both simple heating or under microwave irradiation, precluding therefore the necessity of previous preparations of the intermediates methyl or ethyl oxalic acid esters, and its subsequent transesterification with phenol.

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