

Acetylation and benzylation of various aromatics on sulfated zirconia

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Abstract

Sulfated zirconia (SZ) has been found to have a high performance in the benzylation of anisole. Thus, several aromatics were reacted with benzoic anhydride, benzoyl chloride, and acetic anhydride as acylating agents on SZ, to give the corresponding benzophenones and acetophenones. The rate of the acylation reactions is dependent on the nature of the respective aromatic. The reactivity decreases in the following order: anisole > mesitylene > 3-chloroanisole ~ *m*-xylene ~ 2-chloroanisole > toluene for benzylations on SZ. The application of SZ as a catalyst for the acetylation of aromatics was only successful in case of anisole.

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1. Introduction

Aromatic ketones are valuable intermediates in the production of fine chemicals, which are synthesised mainly by acylation of aromatics with acid chlorides or carboxylic anhydrides. Up to now, stoichiometric or higher amounts of corrosive Lewis acids have been used to activate the acylating agent (Friedel–Crafts acylation). These acids form complexes with the ketones and have to be cleaved by hydrolysis and neutralisation. In view of growing environmental problems the high amount of effluents generated in this process is not tolerable. Accordingly, there are strong efforts to replace the soluble Lewis acids by solid acids. This method might contribute to the development of cleaner techniques in the chemical industry.

Numerous papers report on attempts to turn the aromatic acylation from stoichiometric into catalytic processes. For example the synthesis of benzophenones was achieved in the presence of the homogeneous catalyst triflic acid [1,2]. Moreover, hafnium(IV) triflate proved to be able to catalyse the formation of aromatic ketones, but the use of the required solvent system nitromethane/lithium perchlorate [3,4] is not convenient for industrial application.

Solid acids are attractive catalysts for acylation of aromatics because of their easy separation from the reaction

mixture by filtration. The acylation of anisole using common acylating agents, such as acetic anhydride, was performed over zeolites [5–10], clays [11–13], Nafion-H on silica [14], heteropoly acids [15], and microencapsulated scandium(III) triflate in combination with nitromethane/lithium perchlorate [16]. Furthermore, *m*-xylene was reacted with benzoyl chloride on a silica-bonded perfluoroalkanesulfonic acid [17]. Modified metal oxides like sulfated zirconia (SZ) [18], sulfated alumina [19], Al-promoted SZ [20], Al-promoted sulfated titania [21], and tungsten oxide on zirconia [22] were applied to the benzylation of toluene.

In continuation of our former investigations on the use of SZ as a heterogeneous catalyst [23–26], this paper reports on investigations of (i) the catalytic activity of SZ in comparison with other solid catalysts and (ii) the reactivity of anisole, halogen substituted anisoles, and methylaromatics in their benzylation and acetylation on SZ.

2. Experimental

2.1. Chemicals

Anisole (99.7%, anhydrous), 2-chloroanisole (98%), 3-chloroanisole (98%), mesitylene (98%), *m*-xylene (99%), toluene (99%), acetic anhydride (98%), and benzoyl chloride (99%) were purchased from Aldrich, benzoic anhydride (97%) from Fluka, benzoic acid *n*-butylester (98%) from

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Merck, and phthalic acid dimethyl ester (99%) from Acros Organics. The chemicals were used without further purification. Anisole, mesitylene, *m*-xylene, and toluene have been stored over sodium wire.

Nafion-H (on silica), Amberlyst-15 (dry form) and montmorillonite K-10 were purchased from Aldrich, H-BEA (Si/Al = 25) and H-mordenite (Si/Al = 10) from Süd-Chemie.

2.2. Preparation and characterisation of SZ

The catalyst, SZ, was prepared by adding aqueous ammonia to an aqueous solution of ZrOCl_2 until pH 8 was achieved. The precipitate was filtered, washed several times until free of chloride, dried at 110 °C for 15 h, impregnated with diluted sulfuric acid (10%), filtered again and calcined at 500 °C in air for 1 h. The resulting white solid contained 1.64% sulfur. The catalyst was stored in a desiccator over dry silica gel.

X-ray powder diffraction measurements of SZ were performed using X-ray powder diffraction with Cu $K\alpha$ radiation (RD 7, R. Seifert & Co., Freiberg, Germany). The catalyst exhibited the tetragonal modification of ZrO_2 (PDF-No: 42-1164).

Specific surface areas and pore diameters were measured using nitrogen adsorption at 77 K (ASAP 2000 system, Micromeritics). The acidity of SZ was characterised by temperature programmed desorption (TPD) of ammonia, which was pre-adsorbed at 100 °C. The ammonia desorbed was quantified by reaction with 0.1N sulfuric acid and backtitration.

2.3. Catalytic experiments

2.3.1. Comparison of various solid acids as acylation catalysts

A mixture of 12 ml anisole, 0.00265 mol benzoic anhydride, and 0.1 g benzoic acid *n*-butylester (internal HPLC-standard) was stirred (700 rotations min^{-1}) at 50 °C in a three-neck flask, with thermometer, reflux condenser, and CaCl_2 tube. The catalysts, SZ, H-BEA, H-mordenite (each calcined for 3 h at 500 °C on air), K-10 (calcined for 1 h at 200 °C on air), Nafion-H or Amberlyst-15, (0.2 g), were added. After maintaining the temperature at 50 °C for 3 h, a sample of the suspension, (0.2 ml), was filtered. The filtrate obtained was analysed to determine the yield of the mixture of 4- and 2-methoxybenzophenone formed by means of HPLC (Merck–Hitachi, Japan with a HPLC pump: L-6250; column: RP-18, 7 mm; solvent system: acetonitrile/water 60/40 (v/v); UV-detector: L-7400, $\lambda = 235 \text{ nm}$).

2.3.2. Various acylation reactions of aromatics on SZ catalyst

The experiments were carried out in the same apparatus. Freshly calcined (air, 3 h, 500 °C) SZ, (0.45 g), was added to a heated mixture of 0.15 mol of the aromatic compound and 0.015 mol of the acylating agent under stirring

(700 rotations min^{-1}). The reaction temperature was kept constant. All yields given are related to the acylating agent.

2.3.2.1. Monitoring the ketone formation over the reaction time. Essentially the benzoylation and acetylation experiments were performed as described above. Deviating from the above procedure, the formation of benzophenones and acetophenones was followed up by ^1H NMR spectroscopy. Before starting the experiment with the addition of the SZ catalyst, the inert reference substance phthalic acid dimethyl ester, (0.0075 mol), was given to the mixture of aromatic and acylating agent. After reaction times of 5, 10, 20, 30, 60, 120, and 180 min, samples of the slurry, (0.2 ml), were taken via syringe, filtered (removal of the SZ), concentrated in vacuum (removal of nonreacted aromatic, acetic anhydride, benzoyl chloride, and formed acetic acid), and analysed (solvent: CDCl_3). The distinct CH_3 singlets resulting from the standard substance ($(1,2\text{-CH}_3\text{O}_2\text{C})_2\text{C}_6\text{H}_4$; $\delta = 3.90 \text{ ppm}$) and ketones formed (e.g. $4\text{-CH}_3\text{O-C}_6\text{H}_4\text{-COCH}_3$; $\delta = 3.87 \text{ ppm}$; $2\text{-CH}_3\text{O-C}_6\text{H}_4\text{-COCH}_3$; $\delta = 3.91 \text{ ppm}$; $4\text{-CH}_3\text{O-C}_6\text{H}_4\text{-COC}_6\text{H}_5$; $\delta = 3.85 \text{ ppm}$; $2\text{-CH}_3\text{O-C}_6\text{H}_4\text{-COC}_6\text{H}_5$; $\delta = 3.69 \text{ ppm}$; $2,4,6\text{-(CH}_3)_3\text{-C}_6\text{H}_2\text{-COC}_6\text{H}_5$; $\delta = 2.08, 2.32 \text{ ppm}$; $2,4\text{-(CH}_3)_2\text{-C}_6\text{H}_3\text{-COC}_6\text{H}_5$; $\delta = 2.33, 2.36 \text{ ppm}$; $2,6\text{-(CH}_3)_2\text{-C}_6\text{H}_3\text{-COC}_6\text{H}_5$; $\delta = 2.12 \text{ ppm}$) were used for determining the product yield (peak area integration).

2.3.2.2. Preparative experiments. These acylation experiments were performed without using the above mentioned internal reference substance. After cooling down to room temperature and filtering the catalyst from the reaction mixture, the clear solution was concentrated up in vacuum. In the case of benzoic anhydride as the acylating agent, the benzoic acid formed was removed by diluting the solution with 75 ml diethyl ether followed by extraction with 25 ml of 5% aqueous NaOH (twice) and 25 ml of water (twice). The remaining organic solution was dried with anhydrous Na_2SO_4 , filtered, and again concentrated in vacuum. The resulting crude ketones (in most cases mixtures of isomers) were purified by Kugelrohr distillation and identified by ^1H NMR, ^{13}C NMR spectroscopy (Unity plus 300 MHz, Varian), and GC–MS (MD 800, Thermo).

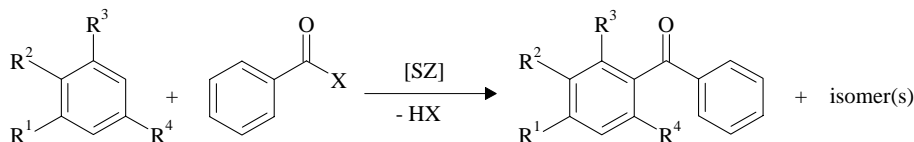
2.4. IR spectroscopic investigations

The infrared spectra were measured on a FTS-60 A spectrometer (Digilab). The samples were transferred into a heatable reaction and pretreatment chamber of a diffuse reflectance attachment (Harrick). Sixty-four scans were accumulated at a resolution of 2 cm^{-1} .

3. Results and discussion

3.1. Catalytic performance of various solid acids

The acylation of anisole with benzoic anhydride (Scheme 1) was used as a test reaction for a comparison of



Scheme 1. SZ-catalysed benzoylation of aromatics. Aromatics: anisole ($R^1 = \text{CH}_3\text{O}$; $R^2\text{--}R^4 = \text{H}$); 2-chloroanisole ($R^1 = \text{CH}_3\text{O}$; $R^2 = \text{Cl}$; $R^3, R^4 = \text{H}$); 3-chloroanisole ($R^1 = \text{CH}_3\text{O}$; $R^2, R^4 = \text{H}$; $R^3 = \text{Cl}$); mesitylene ($R^1, R^3, R^4 = \text{CH}_3$; $R^2 = \text{H}$); *m*-xylene ($R^1, R^3 = \text{CH}_3$; $R^2, R^4 = \text{H}$); toluene ($R^1 = \text{CH}_3$; $R^2\text{--}R^4 = \text{H}$). Benzoylating agents: benzoic anhydride ($X = \text{OCOC}_6\text{H}_5$); benzoyl chloride ($X = \text{Cl}$).

Table 1

Properties and catalytic performance of solid acids in the benzoylation of anisole at 50 °C according to Scheme 1

Catalyst	BET surface area (m ² /g)	Average pore diameter (Å)	Concentration of acid sites according to NH ₃ -TPD (mmol/g)	Yield of 4- and 2-methoxybenzophenone after 3 h (%)
SZ	150	68	0.41	71
Nafion-H	224	220	n.d.	59
Amberlyst-15	38	400	n.d.	48
K-10	233	60	0.28	41
H-BEA	500	7.6 × 6.4 ^a	0.87	13
H-mordenite	400	7.0 × 6.5 ^a	0.76	3

Twelve millilitre anisole, 0.00265 mol benzoic anhydride, 0.2 g catalyst.

^a Channels.

the catalytic performances of commercially available solid acids with that of SZ. According to Table 1, SZ exhibited the best performance for the catalysts investigated. The performance of the catalyst for the acylation of anisole with the sterically demanding benzoic anhydride could be less dependent on the BET surface area and its acidity level, and more dependent on the pore size. The advantage of SZ over the other large pore catalysts is its thermal stability, which allows an easy regeneration by calcination in air at 550 °C [26]. In the following, the catalytic performance of SZ was studied systematically in a series of aromatic acylations.

3.2. Benzoylation of various aromatics on SZ catalyst

Anisole, *m*-xylene, and mesitylene were reacted at 100 °C with benzoic anhydride and benzoyl chloride in presence of SZ (Scheme 1). The results are presented in Fig. 1. The reactivity of the aromatics decreased in the following order: anisole > mesitylene > *m*-xylene with benzoic anhydride. Obviously, the methoxy group of anisole has a stronger activating effect on the aromatic system than the three methyl groups of mesitylene. Thus, the SZ-catalysed benzoylation of anisole is complete after 30 min, whereas the complete benzoylation of mesitylene requires a reaction time of several hours. *m*-Xylene is the least reactive aromatic, resulting in a low ketone yield of about 12% after 180 min.

The reactivity order of the aromatics with benzoic anhydride was the same for the acylating agent benzoyl chloride (Fig. 2). But, mesitylene and especially anisole react slower with benzoyl chloride than with benzoic anhydride. Only 52% of 4- and 2-methoxybenzophenone form in the acylation of anisole with benzoyl chloride after 30 min, whereas the reaction with benzoic anhydride is almost complete within this time. This is a surprising result. Acid chlorides

compared to carboxylic anhydrides reveal a higher carbonyl activity and generally react faster with amines and alcohols.

In order to accelerate the heterogeneously catalysed benzoylation, the reaction temperature was raised from 100 to 136 °C. The effect of the higher temperature on the initial phase of the reactions is represented in Fig. 3. As expected, the ketone yields were improved. Again the same reactivity sequence: anisole > mesitylene > *m*-xylene was found. The aromatics reacted faster with benzoic anhydride than with benzoyl chloride. The only exception was *m*-xylene, which was acylated faster at 136 °C with benzoyl chloride than with benzoic anhydride (ketone yields 12 and 7%, respectively).

To investigate the SZ-catalysed benzoylation in detail, the experiments were extended to chloroanisoles, fluoroanisoles, and toluene. Among the aromatics benzoylated,

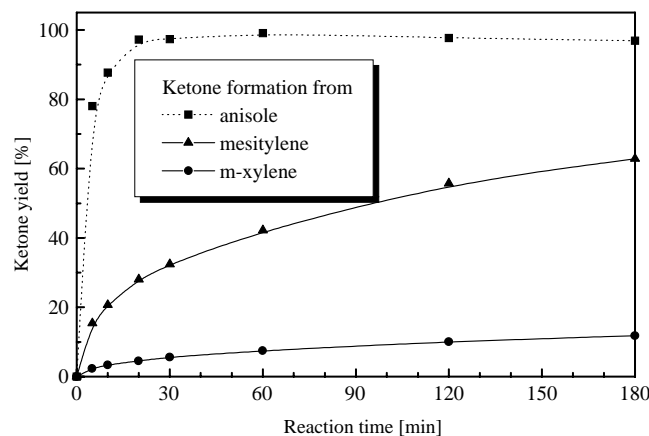


Fig. 1. Kinetics of the SZ-catalysed acylation of aromatics with benzoic anhydride at 100 °C. Formed isomers from anisole: 4-/2- $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{COC}_6\text{H}_5 = 96/4$; mesitylene: 2,4,6-(CH_3)₃- $\text{C}_6\text{H}_2-\text{COC}_6\text{H}_5 = 100$; *m*-xylene: 2,4-/2,6-(CH_3)₂- $\text{C}_6\text{H}_3-\text{COC}_6\text{H}_5 = 90/10$.

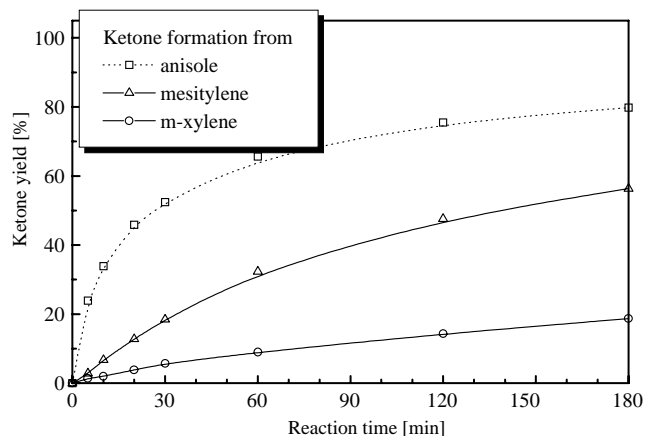


Fig. 2. Kinetics of the SZ-catalysed acylation of aromatics with benzoyl chloride at 100 °C. Formed isomers from anisole: 4-/2-CH₃O-C₆H₄-COC₆H₅ = 94/6; mesitylene: 2,4,6-(CH₃)₃-C₆H₂-COC₆H₅ = 100; *m*-xylene: 2,4-/2,6-(CH₃)₂-C₆H₃-COC₆H₅ = 90/10.

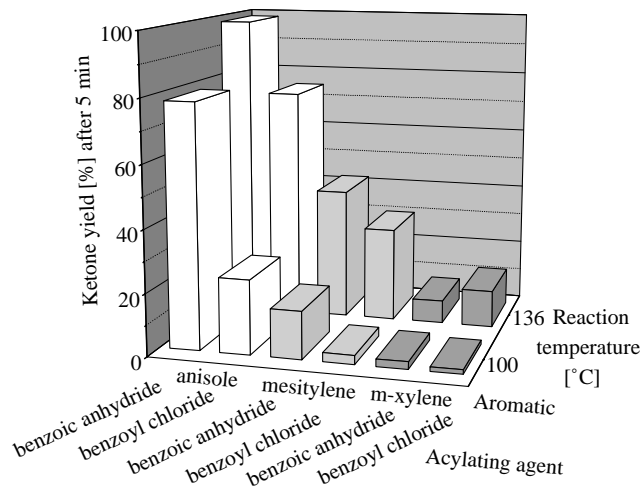


Fig. 3. SZ-catalysed acylation of aromatics: dependence of the initial ketone formation on reaction temperature, acylating agent and aromatic.

anisole and mesitylene exhibited a high, 2-chloroanisole, 3-chloroanisole, and *m*-xylene a moderate, and toluene only a low reactivity (Fig. 4). The aromatic reactivity of anisole is reduced significantly by introducing a chlorine

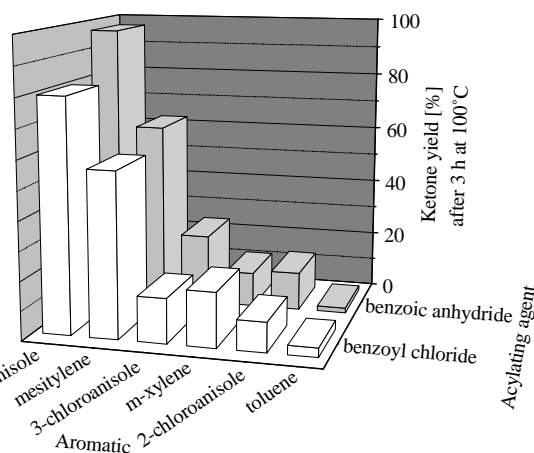


Fig. 4. SZ-catalysed acylation of aromatics: different reactivity of aromatics towards benzoic anhydride and benzoyl chloride.

atom into the aromatic ring. Moreover, 2-fluoroanisole and 3-fluoroanisole did not react with the benzoylating agents used in the presence of SZ. The activation of the aromatic system by the methoxy group is surpassed by the deactivating, strongly electron withdrawing effect of the fluorine atom. The benzylation of 2-fluoroanisole seems only to be possible under Friedel–Crafts conditions [27]. According to Fig. 4, benzoic anhydride was more reactive in the benzylation of anisole, 2-chloroanisole, 3-chloroanisole, and mesitylene than in the benzylation of *m*-xylene and toluene. Unlike that, benzoyl chloride was more reactive in the benzylation of *m*-xylene and toluene.

The results of the benzylation of aromatics on SZ are compiled in Table 2. Compared to the experiments reported in Figs. 1–4, the reaction conditions were modified in most cases, to obtain acceptable ketone yields. The reactions were accelerated by raising the temperature from 100 to 110 °C or 120 °C. The formation of byproducts in the benzylation of chloroanisoles increased with the reaction temperature. The regioselectivity of the benzylation of *m*-xylene decreased from 90/10 to 86/14. Aromatics that exhibited a lower reactivity than anisole and mesitylene could be acylated in presence of higher amounts of SZ. In summary,

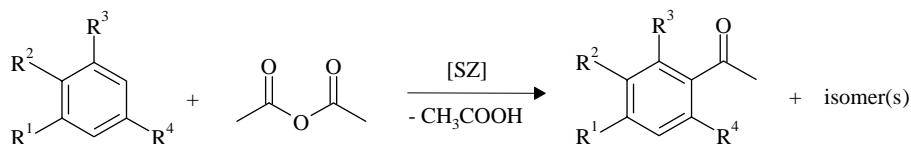
Table 2
SZ-catalysed benzylation of aromatics according to Scheme 1

Aromatic/benzylation agent	Reaction temperature (°C)	Reaction time (h)	Amount of SZ (g)	Reaction product(s)	
				Ketone yield (%)	Isomer(s) (BP = benzophenone)
Anisole/benzoic anhydride	100	1.5	0.45	95	4-CH ₃ O-BP (96), 2-CH ₃ O-BP (4)
Mesitylene/benzoic anhydride	120	5	0.45	95	2,4,6-(CH ₃) ₃ -BP (100)
3-Chloroanisole/benzoic anhydride	120	20	1.687	85 ^a	2-Cl-,4-CH ₃ Ov-BP (84), 4-Cl-,2-CH ₃ O-BP (9), 2-Cl-,6-CH ₃ O-BP (7)
2-Chloroanisole/benzoic anhydride	120	5	1.687	70 ^b	3-Cl-,4-CH ₃ O-BP (100)
<i>m</i> -Xylene/benzoyl chloride	120	5	1.125	88	2,4-(CH ₃) ₂ -BP (86), 2,6-(CH ₃) ₂ -BP (14)
Toluene/benzoyl chloride	110	20	2.812	70	4-CH ₃ -BP (69), 2-CH ₃ -BP (27), 3-CH ₃ -BP (4)

0.15 mol aromatic, 0.015 mol benzoylating agent.

^a Byproduct: about 5% benzoic acid 3-chlorophenyl ester.

^b Byproduct: about 20% benzoic acid 2-chlorophenyl ester.



Scheme 2. SZ-catalysed acetylation of aromatics. Aromatics: anisole ($R^1 = \text{CH}_3\text{O}$; $R^2\text{--}R^4 = \text{H}$); 2-chloroanisole ($R^1 = \text{CH}_3\text{O}$; $R^2 = \text{Cl}$; $R^3, R^4 = \text{H}$); mesitylene ($R^1, R^3, R^4 = \text{CH}_3$; $R^2 = \text{H}$); *m*-xylene ($R^1, R^3 = \text{CH}_3$; $R^2, R^4 = \text{H}$).

SZ achieved high ketone yields in the investigated benzoylation reactions.

Some analogous acylation experiments on other solid catalysts, using the same reactants as in our study, have been reported in the literature. Anisole was reacted with benzoic anhydride on an acidic salt of a heteropoly acid (ketone yield: 85% after 2 h at 154 °C) [15], *m*-xylene with benzoyl chloride on a silica-bonded perfluoroalkanesulfonic acid (conversion of the acylating agent: 89% after 6 h at 140 °C) [17], and toluene with benzoyl chloride on Al-promoted SZ (ketone yield: 93% after 10 h at 110 °C) [20]. To our knowledge, heterogeneously catalysed acylations of chloroanisoles have not yet been published.

3.3. Acetylation of various aromatics on SZ catalyst

Kinetic experiments on the SZ-catalysed acylation of anisole, mesitylene, and *m*-xylene with acetic anhydride (Scheme 2) were carried out analogously to the benzoylation experiments (Scheme 1, Figs. 1 and 2). The aromatics exhibited the same reactivity sequence found for their acylation with benzoic anhydride and benzoyl chloride. Only anisole was converted to the acetophenones in higher yield. In contrast, the acetylation of mesitylene and *m*-xylene stagnated after few minutes at a low level of conversion (Fig. 5). Similar phenomena are reported for the acetylation of toluene [28] on zeolites and heteropoly acids [29]. A product inhibition of the catalyst surface is assumed to be responsible for the incomplete reactions. The low product yield was improved only by increasing the toluene/acetic anhydride ratio [28,30] and by performing the acylation at higher temperature under pressure (steel autoclave, 150 °C) [30].

To identify the possibly inhibiting strongly adsorbed reaction products formed during the acetylation of *m*-xylene and mesitylene (2,4-dimethylacetophenone and 2,4,6-trimethylacetophenone, respectively), further experiments were done.

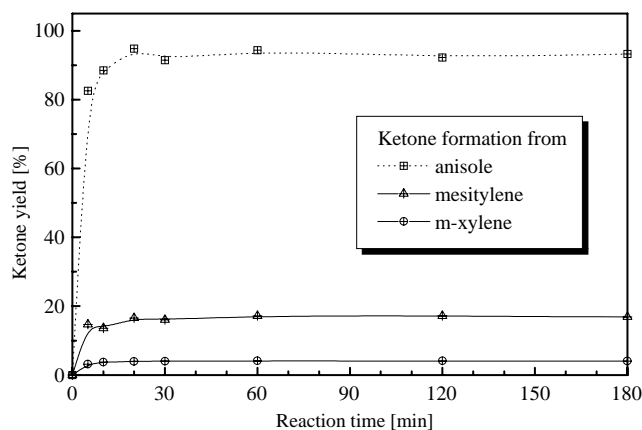


Fig. 5. Kinetics of the SZ-catalysed acylation of aromatics with acetic anhydride at 100 °C. Formed isomers from anisole: 4-/2- $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{COCH}_3 = 98/2$; mesitylene: 2,4,6- $(\text{CH}_3)_3-\text{C}_6\text{H}_2-\text{COCH}_3 = 100$; *m*-xylene: 2,4-/2,6- $(\text{CH}_3)_2-\text{C}_6\text{H}_3-\text{COCH}_3 = 98/2$.

The deactivated SZ catalyst samples from these two reactions (SZ-a, SZ-b) were separated after 15 min from the reaction mixture, thoroughly washed with dichloromethane (five times), and dried at 80 °C in vacuum (5 mbar). Catalytically active SZ was separated from the acetylation of anisole after 2 min and treated in the same manner (SZ-c). In addition, fresh SZ was investigated (SZ-d).

The sulfur content, BET surface area, and pore diameter of the SZ remain almost unchanged after reaction for 2 or 15 min (Table 3). During the acylation experiments, the catalysts became covered with carbonaceous deposits (detected carbon contents: 0.84–0.95 wt.%). However, these deposits do not affect the pore structure of SZ.

The infrared spectra of SZ-a, SZ-b, SZ-c, and SZ-d were compared. For reference, 2,4-dimethylacetophenone, 2,4,6-trimethylacetophenone, and 4-methoxyacetophenone were adsorbed on SZ (spectra SZ-a', SZ-b', and SZ-c'). Fig. 6 shows the region of C=O and C=C stretching vibra-

Table 3
Comparison of the properties of fresh SZ and SZ used in Scheme 2

Catalyst	Aromatic	Reaction time (min)/catalyst state	Sulfur content (wt.%)	Carbon content (wt.%)	BET surface area (m^2/g)	Average pore diameter (Å)
SZ-a	<i>m</i> -Xylene	15/deactivated	1.66	0.95	146	67
SZ-b	Mesitylene	15/deactivated	1.60	0.90	144	68
SZ-c	Anisole	2/active	1.61	0.84	146	67
SZ-d	–	–/active	1.64	–	150	68

0.15 mol aromatic, 0.015 mol acetic anhydride, 0.45 g catalyst, reaction temperature: 100 °C.

Table 4
SZ-catalysed acetylation of aromatics according to Scheme 2

Aromatic	Reaction temperature (°C)	Reaction time (h)	Amount of SZ (g)	Reaction product(s)	
				Ketone yield (%)	Isomer(s) (AP = acetophenone)
Anisole	100	1.5	0.45	91	4-CH ₃ O-AP (98), 2-CH ₃ O-AP (2)
Mesitylene	100	3	1.687	42	2,4,6-(CH ₃) ₃ -AP (100)
2-Chloroanisole	130	20	1.687	36	3-Cl-,4-CH ₃ O-AP (100)
<i>m</i> -Xylene	100	3	1.687	7	2,4-(CH ₃) ₂ -AP (98), 2,6-(CH ₃) ₂ -AP (2)

0.15 mol aromatic, 0.015 mol acetic anhydride.

tions, demonstrating the deposition of carbonaceous species on the surface of the catalysts exposed to the reaction mixture. The band at 1622 cm⁻¹ in the spectrum of SZ-d corresponds to the ending vibration of molecularly adsorbed water. The water was not removed by thermal treatment to protect the spectra of the used catalysts from changes due to decomposition of carbonaceous deposits.

Bands at 1559 and 1465 cm⁻¹ observed in the spectra of all used catalyst samples are assigned to asymmetric and symmetric OCO stretching vibrations of surface acetate complexes formed by reaction of acetic anhydride or acetic acid with basic sites of the zirconia surface.

Unlike catalytically active SZ-c, bands due to carbonyl stretching vibrations at 1743, 1712, and 1645 cm⁻¹ and carbonyl or aromatic ring vibrations at 1611 cm⁻¹ are clearly observed in the spectrum of SZ-a. The carbonyl band of neat 2,4-dimethylacetophenone has been reported at 1682 cm⁻¹ [3]. A shift of this band towards lower wavenumbers may occur by ligation of the carbonyl oxygen to Lewis acid surface sites. For instance, the $\nu(\text{CO})$ of acetophenone and 4-methoxyacetophenone at 1685 and 1664 cm⁻¹, respec-

tively, have been shown to shift to 1635 cm⁻¹ by adsorption on silica-alumina [31]. 2,4-Dimethylacetophenone on SZ displays a peak at 1694 cm⁻¹, which could be assigned to the carbonyl group of the adsorbed ketone (spectrum SZ-a'). The spectrum of SZ-b contains a shoulder near 1696 cm⁻¹, which is close to the carbonyl vibration of free 2,4,6-trimethylacetophenone at 1703 cm⁻¹ [32], and a broad band between 1650 and 1600 cm⁻¹. For the active catalyst SZ-c, the IR evidence of product deposition is even less substantial. Here, the peaks at 1595 and 1502 cm⁻¹ are attributed to anisole, strongly adsorbed on Lewis acid sites via the methoxy group [26].

In summary, IR spectroscopy indicates the presence of carbonyl containing deposits especially on the surface of the catalyst deactivated in the acetylation of *m*-xylene. The result points to a poisoning of active sites by reaction or condensation products.

Further attempts to prepare acetophenones from anisole, mesitylene, 2-chloroanisole, and *m*-xylene on SZ are given in Table 4. Except for anisole, none of the aromatics reacts to the desired products in very high yields. The slightly improved yields of the ketones formed from mesitylene and *m*-xylene are most likely due to the increased catalyst amount (1.687 g). Neither elevated reaction temperatures, nor prolonged reaction times (not mentioned in Table 4) had an additional, beneficial effect on these acetylations.

The problem of low conversion and low product yield in the heterogeneously catalysed acetylation of *m*-xylene cannot be solved by substituting the solid for a homogeneous catalyst. When 1 or 4 mol% of triflic acid (suitable catalyst for benzoylations of aromatics [1,2]) were used instead of SZ, the yield of 2,4-dimethylacetophenone formed was only 23 or 31%, respectively (100 °C, reaction time: 24 h). Generally, the catalytic (homogeneous as well as heterogeneous) acetylation of methylaromatics seems to be hindered.

4. Conclusions

Especially sulfated zirconia, but also montmorillonite K-10, Nafion-H, and Amberlyst-15 as solid catalysts, are more active in the benzoylation of anisole with benzoic anhydride than the zeolites H-BEA and H-mordenite. The mentioned active catalysts are characterised by relatively large pore diameters, which seemingly are advantageous for reactions with the sterically demanding benzoic anhydride.

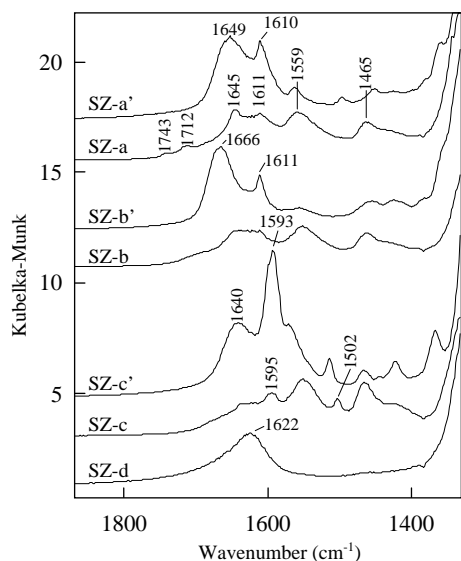


Fig. 6. DRIFT spectra of SZ used in the acetylation of *m*-xylene at 100 °C after 15 min (SZ-a), SZ used in the acetylation of mesitylene at 100 °C after 15 min (SZ-b), SZ used in the acetylation of anisole at 100 °C after 2 min (SZ-c), SZ before reaction (SZ-d), 2,4-dimethylacetophenone on SZ (SZ-a'), 2,4,6-trimethylacetophenone on SZ (SZ-b'), and 4-methoxyacetophenone on SZ (SZ-c').

On SZ, a variety of aromatics (anisole, 2-chloroanisole, 3-chloroanisole, mesitylene, *m*-xylene, toluene) react with benzoic anhydride and benzoyl chloride to the corresponding benzophenones with high yields. As under Friedel–Crafts conditions, the reactivity of the aromatic(s) towards a given acylating agent is influenced by the substituent(s) attached. With a given aromatic, the reaction result also depends on the nature of the benzoylating agent used. Thus, anisole, 2-chloroanisole, 3-chloroanisole, and mesitylene react faster with benzoic anhydride than with benzoyl chloride. *m*-Xylene and toluene exhibit the reverse reaction behaviour. In the literature, the use of true catalysts in the benzoylation of aromatics has been limited to anisole and methylaromatics, up to now. Insofar, with our work we extended the range of successful catalytic benzoylations to chloroanisoles.

The results of the SZ catalysed acetylations of anisole and methylaromatics are in agreement with reported experiments on other heterogeneous catalysts. The acetylation of aromatic ethers is possible on various heterogeneous catalysts, whereas methylaromatics are acetylated with less success. Product inhibition seems to play a negative role in the latter reactions.

On the whole, SZ proved to be a versatile heterogeneous catalyst in aromatic acylations, which in a number of cases can substitute stoichiometric amounts of corrosive and environmentally harmful Lewis acids and, thus, can improve the production of aromatic ketones.

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