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Acylation of naphthalenes and anthracene on sulfated zirconia

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Abstract

Sulfated zirconia (SZ) exhibits a high catalytic performance in the benzoylation of 1-methoxynaphthalene. Therefore, it was used as heterogeneous catalyst in the acylation of methoxynaphthalenes, methylnaphthalenes, naphthalene, and anthracene with benzoic anhydride, benzoyl chloride, and acetic anhydride to synthesize aromatic ketones. The rate of product formation on SZ was dependent on the respective aromatic, on the solvent used, and on the ratio of aromatic to acylating agent.

Keywords: Solid acids; Sulfated zirconia; Naphthalenes; Anthracene; Aromatic acylation; Aromatic ketones

1. Introduction

The acylation of aromatics is the most important process in organic chemistry for the synthesis of aromatic ketones. The target products are intermediates or final compounds used in the production of pharmaceuticals, cosmetics, agrochemicals, dyes, and special chemicals. Currently, strong economic and ecological factors demand the replacement of corrosive Lewis acids, used stoichiometrically to activate the acylating agent (Friedel–Crafts acylation), with heterogeneous acid catalysts. Because of their easy separation from the reaction mixture by filtration, solid acids are attractive acylation catalysts. In the case of their successful application in large-scale processes, the extensive formation of liquid effluents can be avoided.

Numerous papers have reported on the heterogeneously catalyzed acylation of monocyclic aromatics, such as anisole, mesitylene, xylenes, and toluene on zeolites [1–6], clays [7–9], Nafion-H on silica [10], and heteropoly acids [11,12]. Considerably less has been published on the heterogeneously catalyzed acylation of bicyclic aromatics. These publications focus mainly on the synthesis of 2-acetyl-6-methoxynaphthalene, an intermediate for the production of the pharmaceutical Naproxen, from 2-methoxynaphthalene and acetic anhydride on zeolites [13–21]. Further papers have covered the zeolite-catalyzed acetylation and benzoylation of naphthalene [22,23].

In a continuation of our investigations of sulfated zirconia (SZ) as a heterogeneous catalyst in the acylation of monocyclic aromatics [24–28], we studied the acylation of naphthalene, methylnaphthalenes, methoxynaphthalenes, and anthracene on SZ. Additional aspects considered here are (i) the catalytic activity of SZ in comparison with that of other solid catalysts, (ii) the influence of solvents, and (iii) the influence of the aromatic/acylating agent ratio on ketone formation.

2. Experimental

2.1. Chemicals

Naphthalene (99%), 1-methoxynaphthalene (98+%), 2-methoxynaphthalene (99%), 1,3-dimethylnaphthalene (96%), anthracene (99%), acetonitrile (anhydrous, 99.8%),

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chlorobenzene (anhydrous, 99.8%), cyclohexane (anhydrous, 99.5%), 1,2-dichloroethane (anhydrous, 99.8%), nitrobenzene (99+%), acetic anhydride (99+%), benzoyl chloride (99%) were all purchased from Aldrich; benzoic anhydride (97%), 1,2-dimethoxyethane (anhydrous, 99%), and $ZrOCl_2 \cdot 8H_2O$ (> 99%) were from Fluka; 1-methylnaphthalene (97%), 2-methylnaphthalene (99%), $H_3[PW_{12}O_{40}] \times H_2O$ (p.a.), and Cs_2CO_3 (99.5%) were from Acros Organics. The chemicals were used without further purification.

SZ and the following solid acids were investigated: Nafion-H (a perfluoroalkanesulfonic acid polymer) on SiO_2, Amberlyst-15 (an arenesulfonic acid polymer), and Montmorillonite K-10 (a clay mineral) were purchased from Aldrich; H-BEA (a zeolite, Si/Al = 25) and H-mordenite (a zeolite, Si/Al = 10) were from Süd-Chemie; and $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (a heteropoly acid) was prepared according to the method described in [29]. The catalysts were pretreated before experiments. SZ, H-BEA, and H-mordenite were calcined at 500 °C in air for 3 h; $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ was calcined at 300 °C in N_2 for 3 h; K-10 was calcined at 200 °C in air for 1 h; Nafion-H on SiO_2 was calcined at 120 °C in vacuum for 1 h; Amberlyst-15 was stored at room temperature in vacuum over concentrated sulfuric acid.

2.2. *Preparation of SZ and methods of characterization*

The catalyst, SZ, was prepared by the addition of aqueous ammonia to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ 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 wt%), filtered, and calcined at 500 °C in air for 1 h. The resulting white solid contained 1.64 wt% sulfur. The catalyst was stored in a desiccator over dry silica gel.

X-ray powder diffraction measurements of SZ were performed with Cu-K_α 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 with nitrogen adsorption at 77 K (ASAP 2000 system; Micromeritics). The acidities of SZ, K-10, H-BEA, and H-mordenite were characterized by temperature-programmed desorption (TPD) of ammonia (heat conductance detection), which was pre-adsorbed at 100 °C. The ammonia desorbed was quantified by reaction with 0.1 N sulfuric acid and back-titration.

The type and amount of acid sites (Lewis, L, or Brønsted, B) present in the samples relative to one another were studied by the FTIR photoacoustic spectroscopy (FTIR-PAS) of chemisorbed pyridine adsorbate complexes (PACs). Samples were pretreated at 150 °C for 30 min under Ar and then exposed to pyridine twice (2 × 30 µl) at 150 °C with Ar flushing for 15 min in between. The measurements were carried out before and after pyridine adsorption between 4000 and 400 cm^{-1} in a MTEC 300 photoacoustic cell on a Perkin-Elmer FTIR system 2000 spectrometer (H-mordenite: on a Digilab FTS 3000 Spectrometer Excalibur). We normalized the spectra by setting the transmission at 500.35 cm^{-1} of each spectrum to 100% and multiplying the spectrum by the corresponding factor. Brønsted acid sites (B) are indicated by the band at 1550 cm^{-1}. The band at 1490 cm^{-1} can be assigned to PACs bonded to both Brønsted and Lewis acid sites, whereas the bands at 1450 and about 1600 cm^{-1} can be attributed exclusively to Lewis acid sites (L) in the samples. When the 1490 cm^{-1} band intensity is one-third that of the 1450 cm^{-1} band, Lewis acid sites are exclusively present in the sample. When the 1490 cm^{-1} band intensity is higher than that, the sample also possesses Brønsted acid sites.

2.3. *Catalytic experiments*

2.3.1. *General procedure*

The reaction mixture (aromatic, acylating agent, catalyst, and solvent) was stirred (700 rpm) in a 100-ml three-necked flask, with magnetic stirrer, thermometer, reflux condenser, and $CaCl_2$ tube and heated to the reaction temperature. In some experiments the ketone formation was monitored over the reaction time. These experiments were performed with the use of 15 mmol aromatic, 30 mmol acylating agent, 1.125 g SZ, and 30 ml 1,2-dichloroethane. Samples (0.2 ml of the mixture) were taken periodically after 5, 10, 20, 30, 60, 120, and 240 min via syringe, filtered to separate the catalyst, and concentrated in vacuum to remove the solvent and other low boiling compounds (in acetylation reactions: acetic anhydride, acetic acid). All yields given are related to the aromatic.

2.3.2. *Analysis*

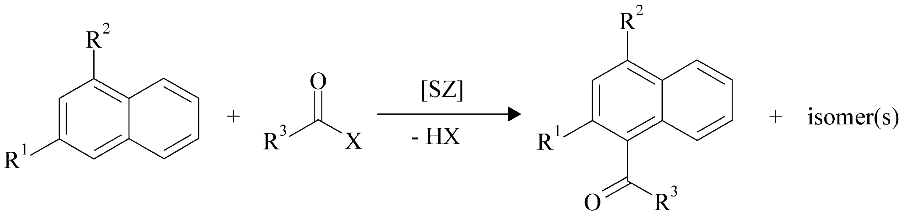
The product yield was determined by ^1H NMR spectroscopy (solvent: $CDCl_3$). To identify and quantify the aromatics to be reacted and aromatic ketones formed, the following signals (singlets) were evaluated.

$C\underline{H}_3O$: 1-methoxynaphthalene 3.97 ppm; 1-benzoyl-4-methoxynaphthalene 4.03 ppm; 1-acetyl-4-methoxynaphthalene 4.02 ppm, ($C\underline{H}_3CO$: 2.68 ppm); 2-methoxynaphthalene 3.90 ppm; 1-benzoyl-2-methoxynaphthalene 3.80 ppm; 1-acetyl-2-methoxynaphthalene 3.94 ppm, ($C\underline{H}_3CO$: 2.63 ppm).

$C\underline{H}_3$: 1-methylnaphthalene 2.68 ppm; 1-benzoyl-4-methylnaphthalene 2.75 ppm; 2-methylnaphthalene 2.47 ppm; 1-benzoyl-2-methylnaphthalene 2.29 ppm; 1.3-dimethylnaphthalene 2.44 ppm, 2.63 ppm; 1-benzoyl-2,4-dimethylnaphthalene 2.26 ppm, 2.71 ppm; 1-acetyl-2,4-dimethylnaphthalene 2.37 ppm, 2.40 ppm, 2.59 ppm (clear identification of the $C\underline{H}_3CO$ signal was not possible).

$\underline{H}^{10}$: anthracene 8.41 ppm (identical to $\underline{H}^9$); 9-benzoylanthracene 8.54 ppm; 9-acetylanthracene 8.47 ppm, ($C\underline{H}_3$ CO: 2.08 ppm).

The ^1H NMR spectra of naphthalene and its acylation products showed no suitable signals for the calculation of the



Scheme 1. SZ-catalyzed acylation of substituted naphthalenes. Aromatics: 1-methoxynaphthalene ($R^1 = H$; $R^2 = CH_3O$); 2-methoxynaphthalene ($R^1 = CH_3O$; $R^2 = H$); 1,3-dimethylnaphthalene (R^1, $R^2 = CH_3$); 1-methylnaphthalene ($R^1 = H$; $R^2 = CH_3$); 2-methylnaphthalene ($R^1 = CH_3$; $R^2 = H$). Acylating agents: benzoic anhydride ($R^3 = C_6H_5$, $X = OCOC_6H_5$); benzoyl chloride ($R^3 = C_6H_5$, $X = Cl$); acetic anhydride ($R^3 = CH_3$, $X = OCOCH_3$).

product yield directly from the reaction mixture. Therefore, the yields of the ketones formed from naphthalene were determined directly from the weights of the isolated products.

2.3.3. *Comparison of various solid acids as acylation catalysts in the benzoylation of 1-methoxynaphthalene*

A mixture of 15 mmol 1-methoxynaphthalene, 15 mmol benzoic anhydride, and 30 ml 1,2-dichlorethane (solvent) was heated to 40 °C. The catalyst (1.125 g) was added to the mixture. After 2 h at 40 °C, a sample was taken as described above and analyzed accordingly.

2.3.4. *Influence of the solvent and the aromatic/acylating agent ratio on the SZ-catalyzed acetylation of 2-methoxynaphthalene*

A mixture of 15 mmol 2-methoxynaphthalene and 15 mmol acetic anhydride was reacted at 70 °C in 30 ml acetonitrile, cyclohexane, 1,2-dichloroethane, 1,2-dimethoxyethane, or nitrobenzene as a solvent on SZ (1.125 g). The reaction mixture was analyzed after a reaction time of 4 h. To investigate the influence of the molar ratio of aromatic to acylating agent on the product formation, the ratio was changed stepwise from 4:1 to 1:4 in further experiments.

2.3.5. *Preparative acylation experiments on SZ*

The experiments were carried out in a 100-ml three-necked flask. The freshly calcined (at 500 °C in air for 3 h) SZ (1.125 g or the respective amount given in the text) was added to a heated stirred mixture of 15 mmol aromatic, 30 mmol acylating agent (acetic anhydride or benzoyl chloride), and 30 ml 1,2-dichloroethane or chlorobenzene. The reaction time was 4 or 20 h. After the mixture was cooled to room temperature and the catalyst was filtered from the reaction mixture, the clear filtrate was concentrated in vacuum. The resulting crude ketones (in some cases isomer mixtures) were purified by Kugelrohr distillation and identified by ^{1}H and ^{13}C NMR spectroscopy (Unity plus 300 MHz; Varian) and GC-MS (MD 800; Thermo). As an exception, crude 9-benzoylanthracene obtained was purified (separation of unreacted anthracene) by means of flash chromatography on silica gel (Kieselgel 60, 230–400 mesh; Merck) with the eluent n-hexane/ethyl acetate (10/1 v/v).

3. Results and discussion

3.1. *Textural properties, acidities, and catalytic performances of various solid acids*

The acylation of 1-methoxynaphthalene with an equimolar amount of benzoic anhydride (Scheme 1) was used as a test reaction for comparison of the catalytic performances of six solid acids with that of SZ. The catalytic results, textural properties, and acidities are listed in Table 1. The results demonstrate complex relationships between catalyst activity, acidity, textural properties, and, probably, the accessibility of active sites.

SZ, $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, Nafion-H on SiO_2, Amberlyst-15, and K-10 are more active than the acidic zeolites, H-BEA and H-mordenite. The acid sites in the narrow zeolite channels are clearly less accessible for the sterically demanding reactants compared with ammonia. Moreover, SZ, Nafion-H on SiO_2, and Amberlyst-15 contain chemical functions, which seem to be especially effective as active sites. The sulfuric and sulfonic acid groups of these catalysts are able to react with acylating agents to give acylsulfates and acylsulfonates, respectively. Acylsulfonates were synthesized and isolated by Effenberger et al. and are very reactive toward aromatics [30]. For SZ, Nafion-H on SiO_2, and Amberlyst-15, a formation of surface-bonded acylsulfates or acylsulfonate surface species as acylating agents in the catalytic cycle can be assumed. The distinct acylating activity of these reagents may be related to their tendency to form surface-bonded sulfate or sulfonate anions as thermodynamically favored leaving groups (Scheme 2). The acylation on $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (acylating species: acyltungstophosphate; leaving group: tungstophosphate anion) could follow a similar mechanism.

The number of acid sites in SZ, Nafion-H on SiO_2, Amberlyst-15, and K-10 does not correlate with their catalytic performances. This is clearly demonstrated by Amberlyst-15, which has the highest number of acid sites (4.70 mmol/g) and exhibits only a moderate catalytic performance. This apparent contradiction can be explained by the exclusive accessibility of the sites in the mesopores. Most of the acid sites are located in the micropores of the polymer network, which are difficult for sterically demanding molecules to reach.

Table 1
Properties and catalytic performances of solid acids in the benzoylation of 1-methoxynaphthalene at 40 °C according to Scheme 1

Catalyst	BET surface area (m^2/g)	Average pore diameter (Å)	Number of acid sites (mmol/g)	Yield of 1-benzoyl-4-methoxy-naphthalene formed after 2 h (%)
SZ	150	68	0.41[c]	50
$Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$	60	72	0.16[d]	40
Nafion-H on SiO_2	224	220	∼ 0.10[e]	22
Amberlyst-15[a]	38	400	4.70[e]	19
K-10	233	60	0.28[c]	13
H-BEA	500	7.6×6.4[b]	0.87[c]	4
H-mordenite	400	7.0×6.5[b]	0.76[c]	3

15 mmol 1-methoxynaphthalene, 15 mmol benzoic anhydride, 1.125 g catalyst, solvent: 30 ml 1,2-dichloroethane.

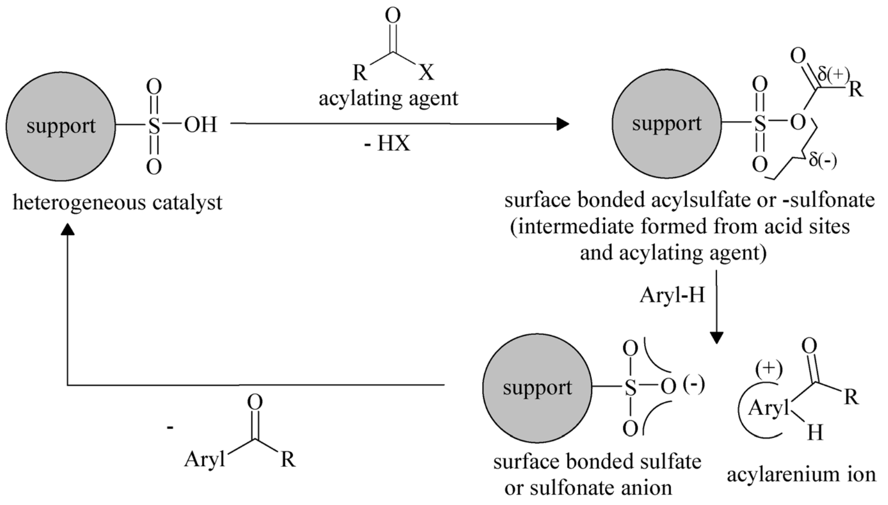
[a] Before reaction: swollen overnight at room temperature in the solvent, start of the reaction by simultaneous addition of acylating agent and aromatic.

[b] Channels.

[c] From ammonia-TPD.

[d] Calculated from the molecular formula.

[e] See product information.



Scheme 2. Possible mechanism of aromatic acylations on heterogeneous catalysts containing sulfate or sulfonate groups such as SZ, Amberlyst-15, and Nafion-H on SiO_2. Acylating agents: benzoic anhydride ($R = C_6H_5$, $X = OCOC_6H_5$); benzoyl chloride ($R = C_6H_5$, $X = Cl$); acetic anhydride ($R = CH_3$, $X = OCOCH_3$).

On the whole, catalytic performance seems to depend (i) on the chemical type and (ii) on the steric availability of the active sites rather than on their amount.

The type of acid sites (Lewis or Brønsted or both) in the samples has been characterized by IR experiments. Fig. 1 shows the IR spectra of the pyridine adsorbate complexes (PACs) formed on the solid acids. The most distinct spectrum is that of the most acidic catalyst, Amberlyst-15, with very broad and strong bands at 1550 and 1490 cm^{-1}, which, in this case, can be attributed to a very high number of Brønsted acid sites. The number of Lewis acid sites in this sample is much lower (weak band at 1450 cm^{-1}). The number of Brønsted acid sites in the other samples decreases in the following order: H-mordenite > SZ (very broad band) > H-BEA > Nafion-H on SiO_2 ≈ K-10, based on the intensities of the band at 1550 cm^{-1}. Lewis acid sites are found in all of the samples (band at 1450 cm^{-1}). From the intensity ratio (1:3) of the 1490 and 1450 cm^{-1} band in Fig. 1, it can be concluded that Nafion-H on SiO_2

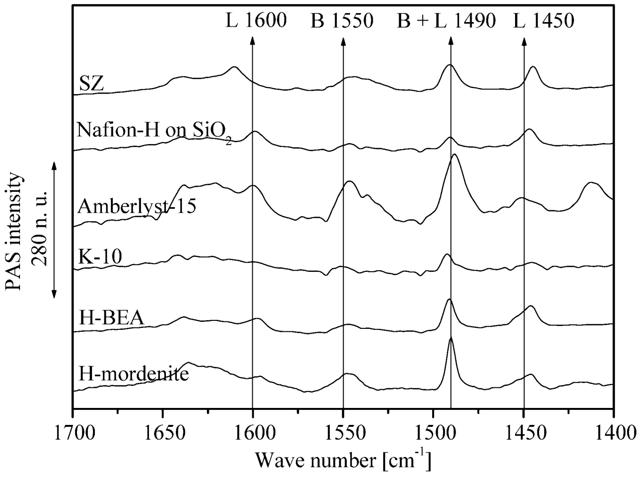


Fig. 1. Photoacoustic FT-IR spectra of pyridine adsorbate complexes (PACs) formed after pyridine adsorption on various solid acids. L, B, and B + L indicates the bands of complexes formed on Lewis, Brønsted or both types of acid sites, respectively.

Table 2
Dependence of the product formation on the nature of the solvent used in the SZ catalyzed acetylation of 2-methoxynaphthalene at 70 °C according to Scheme 1

Solvent	Solvent parameters			Yield of 1-acetyl-2-methoxy/naphthalene formed after 4 h (%)
	Dielectric constant at 25 °C	Acceptor number[a]	Donor number (kcal/mol)[b]	
Cyclohexane	2.0	0	No electron pair donor	62
1,2-Dimethoxyethane	7.0	10.2	24.0	26
1,2-Dichloroethane	10.1	16.7	0	61
Nitrobenzene	34.8	14.8	4.4	67
Acetonitrile	36.0	18.9	14.1	26

Reaction mixture: 15 mmol 2-methoxynaphthalene, 15 mmol acetic anhydride, 1.125 g SZ, 30 ml solvent.

[a] The acceptor number is obtained from the ^{31}P-NMR chemical shift values related to that of the 1:1-adduct $(C_2H_5)_3PO\text{-}SbCl_5$ dissolved in 1,2-dichloroethane.

[b] The donor number has been defined as the negative ΔH value for 1:1-adduct formation between $SbCl_5$ and an electron pair donor solvent in diluted solution in the noncoordinating solvent 1,2-dichloroethane.

contains a low number of Lewis acid sites (SiO_2-support). The Brønsted acid sites in this catalyst (SO_3H-functions in the surface-bonded Nafion) were not detected. Their number seems to be negligible in relation to the Lewis sites of the support. The spectrum of PACs on K-10 shows a band comparable in intensity to that of Nafion-H on SiO_2 at 1490 cm^{-1}, with a much weaker Lewis acid site band at 1450 cm^{-1}. This indicates a minimal amount of Brønsted acid sites for K-10 and practically no Lewis acid sites. The samples SZ, H-mordenite, and H-BEA all have Lewis acid sites (bands at 1450 cm^{-1}) slightly higher in number than those found for Nafion-H on SiO_2. Heteropoly acids such as $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ are known as pure Brønsted acid compounds [12]. For that reason, this catalyst was not investigated by IR spectroscopy.

The interaction of water traces in the reaction mixture and of the acids formed as co-products in the acylation (such as hydrochloric acid, acetic acid, or benzoic acid) with Lewis sites might generate additional Brønsted sites. Therefore, no definitive conclusion can be drawn concerning the contribution of Lewis or Brønsted sites to the catalytic activity of the investigated solid acids.

According to Scheme 2, the aromatic acylation on the sulfur-containing solid acids may be catalyzed by Brønsted acid sites.

An advantage of SZ over the other mesoporous catalysts $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, Amberlyst-15, Nafion-H on SiO_2, and K-10 is its high thermal stability, which permits the removal of deactivating carbonaceous deposits at elevated temperatures. Recently we found that deactivating compounds can be burned off completely from SZ by calcination at 550 °C in air [27]. In contrast, the regeneration of spent heteropoly acids like $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is problematic [12].

The outstanding catalytic suitability of SZ for the benzoylation of 1-methoxynaphthalene correlates with our experiments on the benzoylation of anisole [28]. The acylations reported in the following sections were carried out on the catalyst with the highest performance, SZ.

3.2. *Aromatic acylations on SZ under varied conditions: influence of the nature of the solvent and of the ratio of aromatic to acylating agent*

For the acylation of solid aromatics in liquid phase, the use of solvents is necessary. To identify an appropriate reaction medium for such acylations, the reaction of the solid aromatic 2-methoxynaphthalene with acetic anhydride (Scheme 1) was performed in the presence of various solvents. As seen in Table 2 (solvent parameters from [31]), the heterogeneously catalyzed ketone formation is not influenced by the dielectric constant or the acceptor number of the solvent. It was found that solvents with a low donor number (defined as the negative ΔH value for 1:1 adduct formation between $SbCl_5$ and an electron pair donor solvent in diluted solution in the noncoordinating solvent 1,2-dichloroethane) are the most suitable reaction media. These weak donor solvents cannot interact with the electrophilic acylating species formed on the catalyst surface and do not influence the electrophilic power of the acylating species negatively. The same positive effect of weak donor solvents was found in the synthesis of aromatic ketones under homogeneous (i.e., Friedel–Crafts) conditions. 1,2-Dichloroethane, nitrobenzene, and carbon disulfide are commonly used solvents for aromatic acylation in the presence of $AlCl_3$ or $FeCl_3$. Consequently, it is relevant to the success of the reaction that the solvent be a weak donor, regardless of whether the reaction is homogeneously or heterogeneously catalyzed. All further acylations were performed in the weak donor solvent 1,2-dichloroethane.

An equimolar application would ensure the economic use of expensive aromatics and acylating agents for the aromatic acylations. However, in practice the cheaper reactant is used in excess to accelerate product formation and increase yields. In view of this problem, the educt ratio was optimized for the acetylation of 2-methoxynaphthalene. If the aromatic or the acylating agent is applied in 100% excess, the ketone yield increases from 61 to 77% or 78%, respectively (Fig. 2). A further increase in the threefold amount

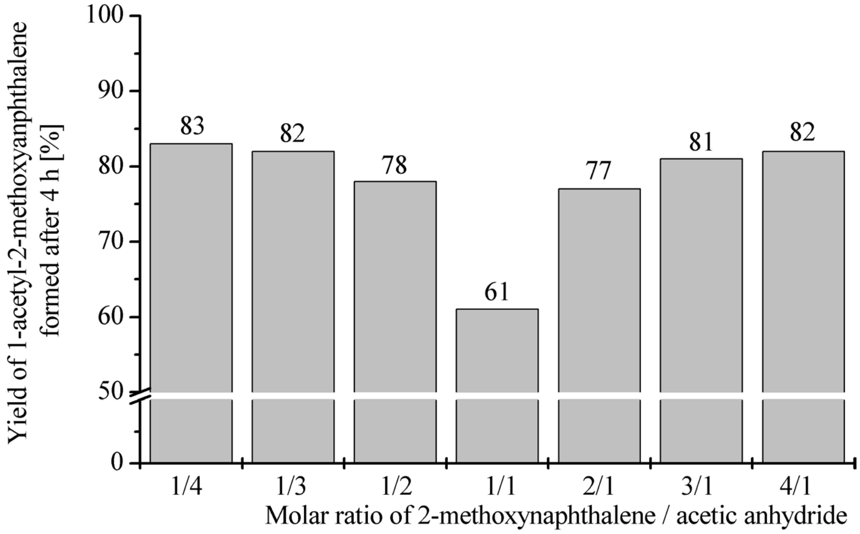


Fig. 2. Dependence of the product formation on the educt ratio in the SZ catalyzed acetylation of 2-methoxynaphthalene at 70 °C according to Scheme 1. Reaction mixture: 2-methoxynaphthalene/acetic anhydride: 1/4 = 15 mmol/60 mmol, 1/3 = 15 mmol/45 mmol, 1/2 = 15 mmol/30 mmol, 1/1 = 15 mmol/15 mmol, 2/1 = 30 mmol/15 mmol, 3/1 = 45 mmol/15 mmol, 4/1 = 60 mmol/15 mmol; 30 ml 1.2-dichloroethane; 1.125 g SZ. The ketone yield is related to the educt which was used in an amount of 15 mmol.

results in additional but lower improvements to 81% (excess of the aromatic) and 82% (excess of the acylating agent). An increase in the educt ratio above 3:1 leads to only marginal effects. In summary, a ratio of two molar equivalents of acylating agent per mole of aromatic was optimal and was applied to the acetylation and benzoylation of various aromatics reported in the following sections.

3.3. *Acylation of different aromatics on SZ at 70 °C*

3.3.1. *Acylation of methoxynapthalenes (Scheme 1)*

1- and 2-Methoxynaphthalene exhibited a similar behavior in the reaction with the acylating agents used (Figs. 3 and 4). 1-Methoxynaphthalene could be acetylated with acetic anhydride and benzoylated with benzoic anhydride on SZ in nearly 100% yield. Benzoyl chloride reacted more slowly and gave only a 82% yield (Fig. 3). The yields of the acylations of 2-methoxynaphthalene did not exceed 85% (Fig. 4). Ketone formation could not be completed by an increase in the SZ amount or the reaction temperature or both or by an extension of the reaction time. As reported, the initial activation of the acylating agent with an equimolar amount of $AlCl_3$ (Friedel–Crafts conditions) before reaction with 2-methoxynaphthaline did also not improve the ketone yield, which remained lower than 85% [32,33]. Hence, the acylation of 2-methoxynaphthaline with carboxylic anhydrides to give 1-acyl-2-methoxynaphthalenes seems to be thermodynamically limited.

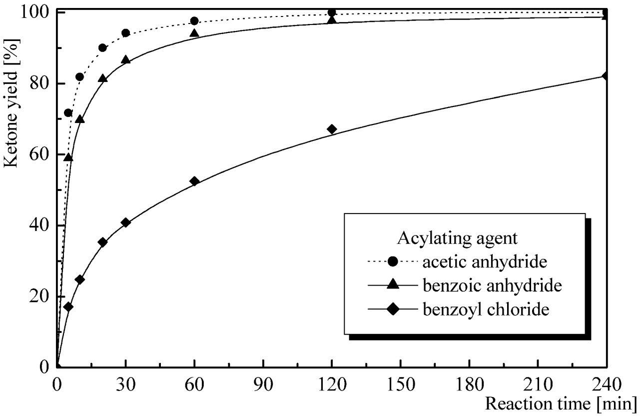


Fig. 3. Kinetics of SZ-catalyzed reactions of 1-methoxynaphthalene with various acylating agents at 70 °C. Products formed: 1-acyl-4-methoxynaphthalenes.

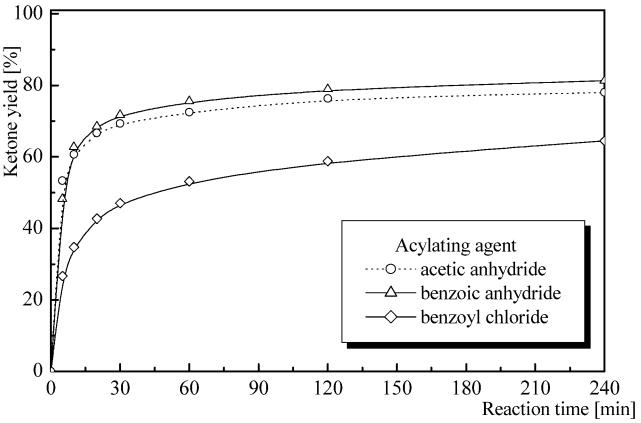


Fig. 4. Kinetics of SZ-catalyzed reactions of 2-methoxynaphthalene with various acylating agents at 70 °C. Products formed: 1-acyl-2-methoxynaphthalenes.

3.3.2. *Acylation of methylnaphthalenes (Scheme 1)*

1,3-Dimethylnaphthalene reacted easily and selectively on SZ with benzoic anhydride and benzoyl chloride to give 1-benzoyl-2,4-dimethylnaphthalene in yields of 93 and 79%, respectively. As in the case of the methoxy-

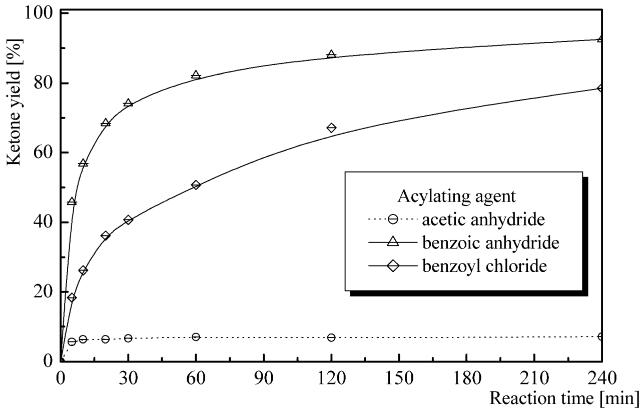


Fig. 5. Kinetics of SZ-catalyzed reactions of 1,3-dimethylnaphthalene with various acylating agents at 70 °C. Products formed: 1-acyl-2,4-dimethylnaphthalenes.

naphthalenes, benzoylation proceeded faster with the carboxylic anhydride than with the acid chloride (Fig. 5). In contrast to that of the methoxynaphthalenes, the acetylation of 1,3-dimethylnaphthalene stagnated within minutes at a low conversion (final ketone yield 7%). Similar phenomena have been found for the acetylation of toluene on H-BEA and heteropoly acids [34,35] and for the acetylation of mesitylene and *m*-xylene on SZ [28]. To the best of our knowledge, true catalytic synthesis of methylacetophenones from methylaromatics on homogeneous or heterogeneous catalysts in acceptable yields has not been reported before. Product inhibition of the acid sites on the catalyst surface is assumed to be responsible for the incomplete reaction [34]. Furthermore, the impossibility of a real catalytic acetylation of methylaromatics may be related to the electronic structure of the reactants. The reactivity of methylaromatics is increased by the weak donating field effect of the methyl group. The resulting mild activation of the aromatic system seems to be sufficient in the case of a catalyzed reaction with the highly stabilized benzoyl cation (delocalization of its positive charge within the aromatic sextet) as the intermediate, but insufficient in the case of the acetyl cation (in which a delocalization of its positive charge is not possible). Therefore, methylacetophenones are not formed in true catalytic reactions, but have to be synthesized according to Friedel–Crafts by stoichiometric activation of the acylating agent.

In Fig. 6, the results of the benzoylation of 1- and 2-methylnaphthalene are compared with those of the other aromatics. In general, 1- and 2-methylnaphthalene were benzoylated considerably more slowly than 1,3-dimethylnaphthalene because of their known lower reactivity. The reaction of 1-methylnaphthaline with benzoic anhydride and benzoyl chloride resulted, respectively, in low yields of 13 and 17% of 1-benzoyl-4-methylnaphthalene. 2-Methylnaphthalene yielded 7 and 12% 1-benzoyl-2-methylnaphthalene with the same two acylating agents, respectively. Neither methylaromatic reacted with acetic anhydride.

3.3.3. Acylation of naphthalene (Scheme 3) and anthracene (Scheme 4)

Owing to the absence of activating substituents, naphthalene is the least reactive of the bicyclic aromatics investigated. Therefore, its acylation with benzoic anhydride and benzoyl chloride on SZ proceeded very slowly to give less than 10% of the target product (Fig. 6). Like 1- and 2-methylnaphthalene, naphthalene was not acylated in the reaction with acetic anhydride.

As expected, the more reactive aromatic, anthracene, was easily and selectively converted on SZ to 9-benzoylanthracene, with yields of 61 and 67% (Fig. 6). In accordance with the benzoylations of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene, benzoyl chloride also revealed a higher reactivity than benzoic anhydride. The low ketone yield of 12% achieved in the reaction of anthracene with

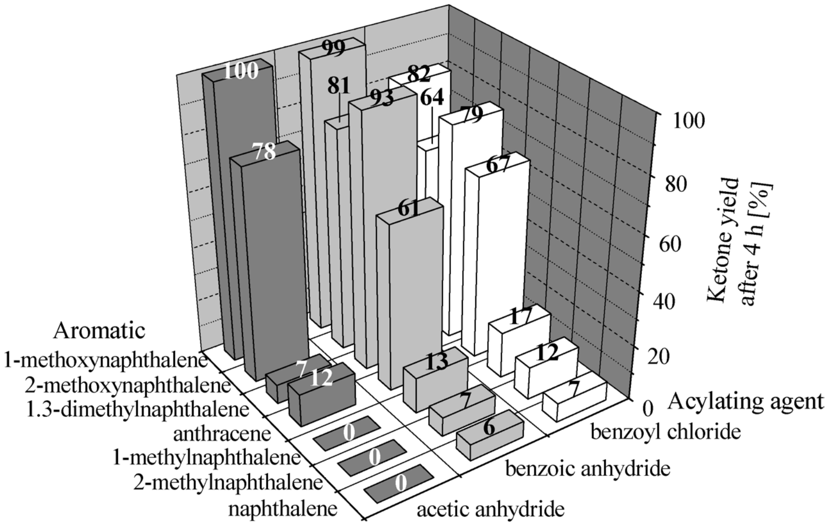
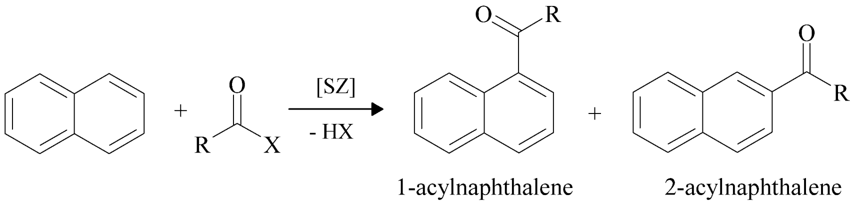
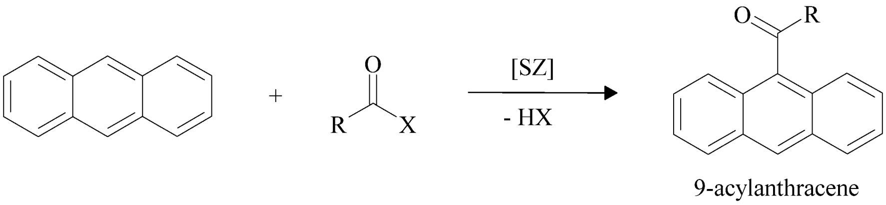


Fig. 6. SZ-catalyzed acylation of substituted naphthalenes, naphthalene, and anthracene at 70 °C. Dependence of the ketone formation on the aromatics and acylation agents used.



Scheme 3. SZ-catalyzed acylation of naphthalene. Acylating agents: benzoic anhydride ($R = C_6H_5$, $X = OCOC_6H_5$); benzoyl chloride ($R = C_6H_5$, $X = Cl$); acetic anhydride ($R = CH_3$, $X = OCOCH_3$).



Scheme 4. SZ-catalyzed acylation of anthracene. Acylating agents: benzoic anhydride ($R = C_6H_5$, $X = OCOC_6H_5$); benzoyl chloride ($R = C_6H_5$, $X = Cl$); acetic anhydride ($R = CH_3$, $X = OCOCH_3$).

acetic anhydride could not be improved by an increased reaction temperature. The reasons for this may be product inhibition of the catalyst or insufficient reactivity of anthracene toward the surface-bonded acetyl intermediate or both.

3.4. Preparative experiments on the synthesis of aromatic ketones on SZ

To develop practical procedures for the synthesis of ketones from naphthalenes and anthracene on SZ, the reaction conditions were optimized. These investigations were concentrated on acetic anhydride and benzoyl chloride as technically relevant acylating agents. The results are listed in Table 3.

A reaction temperature of 70 °C was sufficient for the acetylation and benzoylation of the more reactive aromatics. Moreover, the commonly used catalyst amount of 1.125 g SZ was reduced for the acylation of 1-methoxynaphthalene and 1,3-dimethylnaphthalene to 1-acetyl-4-methoxynaphthalene, 1-benzoyl-4-methoxynaphthalene, and 1-benzoyl-2,4-dimethylnaphthalene. Based on the lower reactivity of benzoyl chloride and to ensure a high conversion of the aromatic, the reaction time was extended to 20 h.

The other aromatics were benzoylated at 120 or 130 °C in chlorobenzene. 1-Methylnaphthalene, 2-methylnaphthalene, and naphthalene gave isomer mixtures of the ketones obtained. With the exception of anthracene, catalyst amounts of more than 1.125 g were needed to achieve acceptable ketone yields. The number of catalytically active sites (determined with ammonia TPD experiments) on SZ in the reaction mixture was substoichiometric (between 2 and 9% of the molar aromatic amount) for all acylations summarized in Table 3.

4. Conclusions

Sulfated zirconia is an efficient catalyst for the reaction of 1-methoxynaphthalene with benzoic anhydride as a sterically demanding acylating agent. Here it exhibits a higher catalytic performance than other solid acids with mesopores, such as $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, Nafion-H on SiO_2, Amberlyst-15, and K-10. These results are consistent with our experiments on the benzoylation of anisole. The low catalytic performances of H-BEA and H-mordenite in the benzoylation of 1-methoxynaphthalene are probably due to the lower accessibility of their acid sites in the narrow channels of the zeolite lattices. The formation of very reactive acylating species and thermodynamically favored leaving groups on their surface may explain the moderate to high catalytic performances of Amberlyst-15, Nafion-H on SiO_2, $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, and SZ.

A considerable influence of the solvent on the product formation was demonstrated for the acetylation of 2-methoxynaphthalene on SZ to 1-acetyl-2-methoxynaphthalene. As found earlier in Friedel–Crafts aromatic acylations, the use of solvents with low donor numbers is also advantageous to the heterogeneously catalyzed acylation.

A molar ratio for 2-methoxynaphthalene and acetic anhydride in the range between 2 and 3 (1:2 and 1:3) is sufficient to achieve fast ketone formation with high yields.

Among the aromatic acylations investigated, the acetylation and benzoylation of 1-methoxynaphthalene and 2-methoxynaphthalene and, furthermore, the benzoylation of 1,3-dimethylnaphthalene and anthracene can be carried out with high ketone yields and on low SZ quantities.

In summary, the application of the heterogeneous catalyst SZ for the synthesis of aromatic ketones was extended from monocyclic aromatics to anthracene and various naphthalenes. SZ amounts with a substoichiometric number of

Table 3
SZ-catalyzed acylation of substituted naphthalenes, naphthalene, and anthracene under optimized reaction conditions according to Schemes 1, 2, and 3, respectively

Aromatic/ acylating agent	Reaction temperature (°C)/ solvent	Reaction time (h)	Amount of SZ (g)	Isolated and purified ketone(s)	
				Yield (%)	Isomer(s) (Isomer ratio) (%)
1-Methoxynaphthalene/ Acetic anhydride	70/ 1,2-Dichloroethane	4	0.75	98	1-Acetyl-4-methoxy-naphthalene (100)
1-Methoxynaphthalene/ Benzoyl chloride	70/ 1,2-Dichloroethane	20	0.9	93	1-Benzoyl-4-methoxy-naphthalene (100)
2-Methoxynaphthalene/ Acetic anhydride	70/ 1,2-Dichloroethane	4	1.125	74	1-Acetyl-2-methoxy-naphthalene (100)
2-Methoxynaphthalene/ Benzoyl chloride	70/ 1,2-Dichloroethane	20	1.125	74	1-Benzoyl-2-methoxy-naphthalene (100)
1,3-Dimethylnaphthalene/ Benzoyl chloride	70/ 1,2-Dichloroethane	20	0.9	84	1-Benzoyl-2,4-dimethylnaphthalene (100)
1-Methylnaphthalene/ Benzoyl chloride	130/ Chlorobenzene	20	2.25	53	1-Benzoyl-4-methyl-naphthalene (92), 2 further isomers[a]
2-Methylnaphthalene/ Benzoyl chloride	130/ Chlorobenzene	20	2.25	81	1-Benzoyl-2-methyl-naphthalene (74), 6 further isomers[b]
Naphthalene/ Benzoyl chloride	130/ Chlorobenzene	20	3.375	69	1-Benzoylnaphthalene/ 2-Benzoylnaphthalene (82/18)
Anthracene/ Benzoyl chloride	120/ Chlorobenzene	4	1.125	89	9-Benzoylanthracene (100)

15 mmol aromatic, 30 mmol acylating agent, 30 ml solvent.

[a] 4/4.

[b] 13/5/4/2/1/1. The isomers formed in minor amounts were identified by their molpeaks (GC-MS analysis). A more precise characterization of these ketones was not possible.

catalytically active surface sites can be used as an alternative to stoichiometric amounts of corrosive and ecologically harmful Lewis acids in acylations of polycyclic aromatics.

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