Friedel Crafts acylation of aromatic compounds over arenesulfonic containing mesostructured SBA-15 materials

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Abstract

Arenesulfonic modified mesostructured SBA-15 is shown as an active catalyst for acylation of aromatic compounds using acetic anhydride as acylating agent. The arenesulfonic acid-centers located within the mesostructured SBA-15 show a greater reaction rate (normalised on the concentration of sulfonic groups) as compared to other sulfonated catalysts and even in solventless conditions. This high activity is accompanied with a remarkable stability without leaching of sulphur species during the reaction. Moreover, an increase of the amount of acid centres does not modify the activity of the material per acid center. Thus, this work introduces a new application of these sulfonated mesostructured materials, not described in literature up to now, and in an important organic reaction.

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Friedel Crafts acylation is one of the most important reactions in organic chemistry for synthesizing aromatic ketones, which are important intermediates for the production of fine chemicals. The conventional stoichiometric catalysts traditionally used e.g. $AlCl_3$, BF_3 or HF present serious drawbacks. In this context, heterogeneous catalysts seem to be an attractive alternative to the homogeneous reaction. Mainly zeolites, exchanged clays, Nafion/silica composites and even grafite have been tested as heterogeneous acylation catalysts over different substrates and using a wide range of acylating agents [1]. New kind of acid solids have recently emerged based on propyl-sulfonic groups anchored to the pore surface of mesostructured MCM-41 [2-3], HMS [4] and SBA-15 [5] materials. This sulfonated mesoporous silicas lead to materials with high surface area, a narrow pore sizes distribution with a high accesibility of acid centers and relative high acid strength. Moreover, the presence of aromatic groups close to the sulfonic acid group has allowed increasing the acid strength of these acid catalysts as compared to propyl-sulfonic modified samples [6-7]. However the catalytic application of these new catalysts has been mainly addressed to esterification [2-4, 8-9] condensation [2-4] and even etherifications [10] reactions being their application in Fine Chemistry processes poor dealt in literature.

In this communication we describe the outstanding activity of these arenesulfonic modified SBA-15 materials (Ar-SO$_3$H) for acylation processes. The activity of this material has been compared with other conventional acid solid catalysts as well as propylsulfonic modified SBA-15 materials (Pr-SO$_3$H). Table 1 lists the main physicochemical properties of the catalysts tested in the acylation process whereas Table 2 shows their catalytic activity for the acylation of anisole in presence of anhydride acetic as acylating agent under different reaction conditions. Both sulfonic

modified mesostructured SBA-15 materials were synthesized using a direct synthesis procedure elsewhere described [5-6].

As expected, no conversion of anisole was observed in the presence of pure silica SBA-15 (entry 1; Table 2). Arenesulfonic containing SBA-15 (entries 2 and 3; Table 2) showed higher absolute conversion of anisole than that of conventional acid zeolites (entries 6 and 7; Table 2). As expected, the increase of temperature leads to an enhancement of the conversion, but the selectivity remains almost constant (entries 2, 11 and 12, Table 2). Note that the selectivity towards p-methoxyacetophenone was higher than 95 % for all the catalysts regardless of the pore size. This fact confirms that this high selectivity is not due to shape selectivity effects but rather to the reaction mechanism (electrophilic susbstitution).

The nature and properties of solvent play an essential role in the reaction rates and selectivities for liquid phase reactions. Acylation of anisole has been carried out in presence of conventional solvents used in this kind of processes over arenesulfonic SBA−15 as catalyst (entries 8,9 and 10, Table 2). Polar solvent such as nitrobenzene (dielectric constant of 35.0) led to higher activity as compared to less polar solvents such as dicholoromethane and toluene (dielectric constants of 8.9 and 2.4, respectively). It is noteworthy that solventless reaction (entry 2, Table 2) showed similar anisole conversion to that obtained with nitrobenzene. This latter result indicates that the presence of solvent is not necessary to obtain good yields when arenesulfonic modified catalysts are used as catalysts. The nature of solvent seems not to have a significant influence on the selectivity.

In order to obtain a quantitative comparison of the catalytic performance of the different sulfonated catalysts, the specific catalytic activity per acid center (the turnover number, TON) has been evaluated and monitored with the reaction time for the acylation of anisole using acetic anhydride as acylating agent (Figure 1). With the purpose of comparison, methane sulfonic acid (CH_3SO_3H) has been employed as a homogeneous reference catalyst. Arenesulfonic containing SBA-15 materials (entries 2 and 3, Table 2) display the highest rate of anisole conversion per acid center as compared to the other catalysts. Note that an increase of the number of active centers per gram of material did not change appreciable the reaction rates. Propylsulfonic modified SBA-15 materials (entry 4, Table 2) gave a low activity evidencing the crucial importance of aromatic group attached close to the sulfonic group for increasing the acid strength necessary for this particular reaction. The significant decrease of conversion rate per acid center observed with Amberlyst could be related to the low accesibility of the acid centers. Finally, homogeneous catalyst evidenced a very poor activity. These catalytic results demonstrate beyond any doubt the high accesibility of acid centers for these arenesulfonic modified mesostructured materials even with acid capacities close to 2.9 mmol H^+ per g of SiO_2.

For the highly active catalysts deactivation occurs after 3 hours of reaction (see Fig. 1). Elemental analysis of catalyst $ArSO_3H^1$, before reaction, indicated 16.7 mmol of C and 1.66 mmol of S per g of dry SiO_2, respectively. After reaction (entry 2, Table 2), these values were 73.3 mmol of C and 1.68 mmol of S. These analysis indicate that the decrease of conversion rate after 3 hours of reaction cannot be attributed to the leaching of active centers, but it is mainly due to the catalysts poisoning by strong organic adsorption. These results would be in agreement with those reported by Rohan

et al.[10] who claim that the causes of deactivation of heterogeneous catalysts in anisole acylation is due to both pore blockage by entrapped polyacylated compounds and no-desorption of the formed p–methoxyacetophenone. Moreover, the amount of these organic deposits correlate perfectly with the reaction temperature. Elemental analysis of carbon retained in the catalyst after reaction at different temperatures (entries 2, 11 and 12) reveal a gradual increase of this value up to 214.6 mmol of C per g of dry SiO_2 at 150 ℃. The change of catalyst's colour after reaction from light yellow (100 ℃) to dark brown (150 ℃) is also an indication of a higher formation of polyacylated compounds.

To remark the catalytic performance of this material, a bulkier substrate such as 2-methoxy-naphthalene (2MN) has been acetylated in presence of acetic anhydride being the results shown in Table 3. Data in Table 3 reveal the high activity of these materials during the two first hours of reaction. This outstanding activity is achieved even in absence of solvent. Acylation of 2MN over Ar-SO_3H[1] catalyst yielded mainly four isomers 1-acetyl-2-methoxy-naphtalene (I), 8-acetyl-2-methoxynaphtalene (II) , 3-acetyl-2-methoxynaphtalene (III) and 6-acetyl-2-methoxynaphtalene (IV) being their molar distribution depicted in Table 3. Unfortunately, this material catalyzes preferentially the formation of isomer I with the selectivity remaining constant along the reaction time. However, the simultaneous formation of isomer IV, which is the desired product (precursor of naproxen), is very low. These results are in contrast with those reported by Guisnet et al. [11] where the acylation of 2MN over HBEA is followed by secondary reactions of isomer I preferentially into isomer IV for long reaction times. Nevertheless, it must be pointed out that the experiment mentioned above was carried out with an excess of 2MN (molar ratio 2MN to acetic anhydride of 5) whereas in this work the reaction was performed with an excess of acylating agent. Indeed, as

concluded by Guisnet et al., an excess of 2MN is necessary to favour an intramolecular mechanism of transacylation of isomer I to isomer IV.

In conclusion, arenesulfonic modified mesostructured materials evidence a high activity in acylation processes accompanied with negligible leaching of sulfur species. This novel material could constitute a competitive alternative to traditional homogeneous systems conventionally used as catalysts in acylation processes. Moreover, such materials can be interesting alternatives to commercially available sulphonated resins (Amberlyst-15 and Nafion) which have low surface areas and poor thermal stability and also used in acylation processes. In this sense, Hoeldrich and co-workers [13] have prepared Nafion/silica composite to increase the accessibility of acid centers and this material showed better activity that the original material (Nafion) for acylation of aromatic compounds. However, no data were presented concerning with the leaching of sulphur species. The arenesulfonic modified SBA-15 materials described in this work possess similar nature of the acid centers and did not evidence any loss of sulphur species during the acylation reaction.

Deactivation and regeneration of this catalyst as well as their catalytic behaviour in lesser activated aromatic compounds to settle its potential industrial applicability are currently under investigation.

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Table 1. Physicochemical properties of catalysts

Sample	S content[a] / mmol [g SiO$_2$]$^{-1}$	Acid capacity[b] / mmol H$^+$[g SiO$_2$]$^{-1}$	Si/Al	BET surface/ m^2 g^{-1}
Ar-SO$_3$H[1]	1.7	1.7	-	720
Ar-SO$_3$H[2]	2.9	2.9	-	733
Pr-SO$_3$H	1.6	1.6	-	666
Amberlyst	-	4.8[c]	-	45
Beta-zeolite	-	-	100	550
H-ZSM-5	-	-	30	490

[a] Elemental analysis by means of HCNS analyzer [b] Acid-base titration using Na$^+$ as exchange cation [c] Acid capacity per g of material.

Table 2. Acylation of anisole over different catalysts and conditions in a batch reactor [a].

Entry	Catalyst	Solvent	T (°C)	Conversion (%)[b]	*p*-Selectivity (%)[b]
1	SBA-15	-	125	-	-
2	Ar-SO$_3$H^1	-	125	24.0	95.2
3	Ar-SO$_3$H^2	-	125	29.8	95.5
4	Pr-SO$_3$H	-	125	1.0	95.4
5	Amberlyst	-	125	57.8	95.7
6	Beta-zeolite	-	125	16.2	100.0
7	H-ZSM-5	-	125	17.2	97.1
8	Ar-SO$_3$H^1	Nitrobenzene	125	24.0	95.2
9	Ar-SO$_3$H^1	Dichloromethane	125	14.0	94.5
10	Ar-SO$_3$H^1	Toluene	125	17.5	93.9
11	Ar-SO$_3$H^1	-	150	31.0	91.8
12	Ar-SO$_3$H^1	-	100	12.5	95.6

[a] *Reagents*: Anisole (185 mmol), Acetic anhydride (196 mmol), Catalyst (0.5 g) and solvent (40 g). [b] Absolute anisole conversion and selectivity towards *p*-methoxyacetophenone after 3 hours of reaction.

Table 3. 2-methoxynaphtalene (2MN) conversion and molar distribution of acetylmethoxynaphtalene isomers at 125 ºC over arenesulfonic modified SBA-15 in a batch reactor[a].

Solvent	Reaction time / h	X_{2MN}[b] (%)	I	II	III	IV
Solventless	0.5	0.5	100	0.0	0.0	0.0
	1	43.3	95.0	1.0	1.3	2.7
	1.5	77.4	94.3	1.3	1.5	2.9
	2	88.5	94.8	1.2	1.4	2.6
	3	89.5	94.9	1.2	1.4	2.5
	8	89.6	94.4	1.4	1.8	2.4
Nitrobenzene	0.5	2.9	96.3	0.0	0.0	3.7
	1	35.0	95.6	0.9	0.8	2.7
	1.5	70.3	94.7	1.0	0.7	3.6
	2	75.2	95.4	1.1	0.6	2.9
	3	79.0	95.4	1.2	0.6	2.8
	8	81.3	95.4	1.2	0.6	2.8

[a] *Reagents*: 2MN (82 mmol), Acetic anhydride (196 mmol), Catalyst (0.5 g) and solvent (40 g).
[b] Absolute conversion of 2 MN

Figure captions

Figure 1. TON of the different sulfonic modified catalysts for the acylation of anisole at 125 ºC in absence of sovent. TON defined as mmol of converted anisole per mmol of sulfonic group.