

**Fries rearrangement of phenyl acetate over sulfonic modified mesostructured
SBA-15 materials**

Rafael van Grieken^{*}, Juan A. Melero and Gabriel Morales

Department of Chemical and Environmental Technology

ESCET

Rey Juan Carlos University

C/ Tulipán s/n, 28933, Móstoles, Madrid, Spain.

Published on:

Applied Catalysis A: General 289 (2005) 143-152

[doi:10.1016/j.apcata.2005.04.059](https://doi.org/10.1016/j.apcata.2005.04.059)

*Corresponding author.

Tel: +34 91 488 70 07. Fax: +34 91 488 70 68

e-mail address: rafael.vangrieken@urjc.es

Abstract

Arenesulfonic modified mesostructured SBA-15 is shown as an active catalyst in the liquid-phase Fries rearrangement of phenyl acetate. The arenesulfonic acid-centers located within the structure of SBA-15 show high catalytic performance as compared to other homogeneous and heterogeneous acid catalysts. This high activity is accompanied with a remarkable stability without leaching of sulphur species during the reaction. Reaction conditions have been investigated in order to optimize production of hydroxyacetophenones. Strong adsorption of reaction products and/or coke deposition on the sulfonic acid sites rapidly deactivates the catalyst. Interestingly, when dichloromethane is used as solvent the deactivation process is slowed down drastically. Finally, this contribution supports a new application of these sulfonated mesostructured materials in the production of fine chemicals.

Keywords: Fries rearrangement, phenyl acetate, Sulfonic acid, SBA-15 and hydroxyacetophenones.

1. Introduction

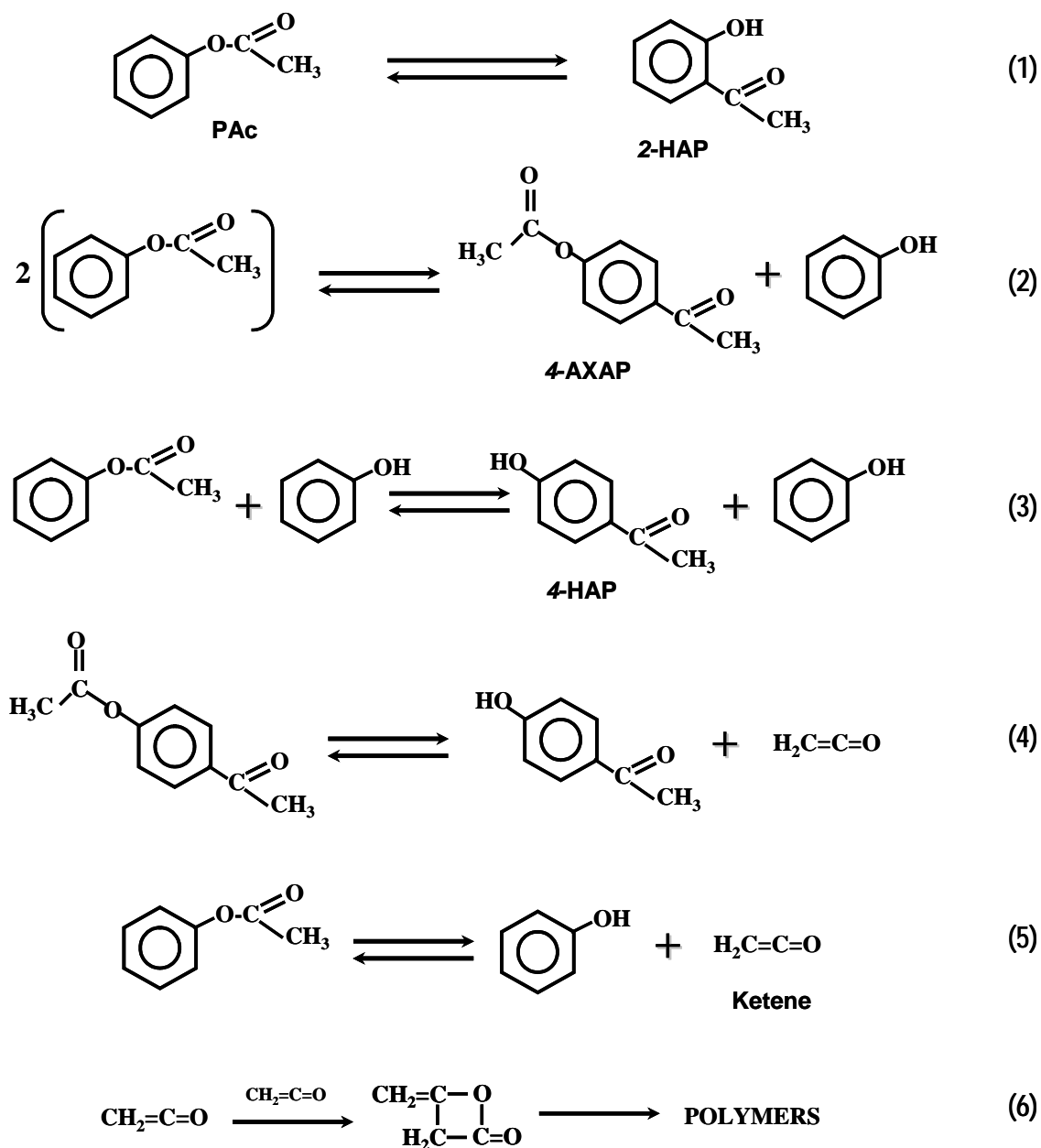
The selective Fries rearrangement of aromatic alcohols esters serves as a valuable synthesis step in the production of industrial pharmaceuticals, dyes and agrochemicals [1]. This reaction involves acylium ion intermediates that are generated from the ester by interaction with an acid catalyst. More specifically, the Fries rearrangement of phenyl acetate (PAC) yields ortho- and para-hydroxyacetophenones (2-HAP and 4-HAP) which are very valuable precursors in the pharmaceutical industry, being this reaction the first step of the Hoechst Celanese manufacturing process of paracetamol [2]. Scheme 1 shows a simplified reaction network for the Fries isomerization of phenyl acetate. Phenol, 2-HAP and *p*-acetoxyacetophenone (4-AXAP) are considered to be primary products, 2-HAP being formed by intramolecular rearrangement of PAC (reaction 1) and 4-AXAP and phenol by the PAC self-acylation (reaction 2). In contrast, 4-HAP appears to be a secondary product formed by two different pathways: intermolecular acylation of phenol with PAC (reaction 3) or dissociation of 4-AXAP (reaction 4) [3 and references therein]. Reactive intermediates such as ketenes are also formed (reactions 4 and 5), and they are supposed to be the main responsible of catalyst deactivation by coke formation (reaction 6).

Conventional homogeneous catalysts such as Lewis acids (AlCl_3 , complexed BF_3) or mineral acids (HF or H_2SO_4) widely used in this reaction have serious drawbacks. The replacement of these conventional catalysts by heterogeneous reusable acid catalysts is promoting an important effort in heterogeneous catalysis research, mainly in the field of zeolites. Zeolites [4-10] and other acid heterogeneous catalysts such as the sulfonic resin Nafion [9] **have been studied** as catalytic systems in the Fries rearrangement of phenyl acetate. Rapid deactivation observed in zeolites, either in gaseous or liquid phase, evidence the need for a greater size pore system. On the other hand, sulfonic

resins such as Nafion or Amberlyst have limited specific surface areas ($<1 \text{ m}^2/\text{g}$ and $45 \text{ m}^2/\text{g}$ respectively) and relatively low thermal stabilities due to their organic nature. Supporting these sulfonic resins over silica with high specific surface has been also tested [4]. More recently [11], commercial pentasil-type zeolite has been reported as a new environment-friendly catalyst in the vapour-phase Fries rearrangement, with better catalytic performances than other zeolites and with the possibility of complete recovery of surface area and catalytic activity upon calcination of the deactivated catalyst. Likewise, heteropoly acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ has been shown as a novel efficient reusable catalyst for Fries rearrangement of phenyl acetate in homogeneous or heterogeneous liquid-phase systems [12-13], evidencing the importance of high acid strength to carry out this reaction. Efforts have also been addressed in the field of homogeneous catalysis: methanesulfonic acid [14] has been evaluated as an environmental-friendly catalyst due to its biodegradability, but the high amount of required catalyst ($>80 \text{ wt. } \%$) to obtain acceptable conversions and selectivities still would keep the problem of waste volume. Nevertheless, research efforts to find recyclable and environmentally benign solid acid catalysts for promoting the liquid-phase synthesis of aromatic ketones from phenyl acetate must be explored.

New kind of acid solids have emerged in the last years based on sulfonic groups contained in mesostructured MCM-41 [15-21] and SBA-15 materials [22-23]. This sulfonated mesoporous silicas lead to materials with high surface area, narrow pore size distribution with high accessibility of acid centres and relative high acid strength. Moreover, the interaction between sulfonic groups covalently attached to the walls of mesostructured silica is stronger than that of active species supported over silica, and hence sulphur leaching may not likely occur. However, the use of this new kind of sulfonic catalyst has been mainly addressed to esterification and condensation reactions

[15-21], being their application in organic reactions related with Fine Chemistry quite limited up to the moment [24-26].



Scheme 1. Reaction network of phenyl acetate Fries rearrangement

The feasibility of tuning the acid strength of the sulfonic groups by close attachment of different moieties might increase their catalytic performance in the Fries rearrangement of phenyl acetate. We have shown earlier in a short communication that the presence of a phenyl group close to the sulfonic group significantly increases the acid strength in comparison to other environments such as methyl groups and hence, an enhancement of catalytic activity in acid-catalysed reactions is expected. In particular, this fact has been clearly evidenced in the anisole acylation with acetic anhydride [24], the esterification of fatty acids [27] and the synthesis of bisphenol-A [28]. Moreover, the catalytic behaviour of arenesulfonic modified SBA-15 materials was briefly described in liquid-phase Fries rearrangement of phenyl acetate in a previous work [23].

Herein, a detailed study on the catalytic performance of these sulfonic modified SBA-15 materials on the liquid phase Fries rearrangement is carried out. Attention was brought on the comparison of their catalytic properties with other acid catalysts as well as the optimization of the reaction conditions.

2. Experimental

2.1 Catalysts preparation

Sulfonic modified mesoporous silica materials. Propyl-sulfonic functionalized SBA-15 (S-1 sample) was synthesized in presence of Pluronic 123 (**a non-ionic block-copolymer comprising EO₇₀PO₂₀EO₇₀; Aldrich**) using tetraethylorthosilicate (TEOS, Aldrich) and mercaptopropyltrimethoxysilane (MPTMS, Aldrich) as described elsewhere [22]. The molar composition of the mixture for 4 g of copolymer was: 0.0369 TEOS: 0.0041 MPTMS: 0.0369 H₂O₂ : 0.24 HCl: \approx 6.67 H₂O. Arenesulfonic functionalized mesoporous SBA-15 materials (S-2 and S-3 samples) were synthesised in presence of Pluronic 123 using TEOS and **chlorosulfonyl-phenylethyl-**

trimethoxysilane (CSPTMS, Gelest) following the procedure of Melero et al. [23]. The molar composition of the mixture for 4 g of polymer was: $(0.0369 - X)$ TEOS: $(0.0041 + X)$ CSPTMS: 0.24 HCl: ≈ 6.67 H₂O. The amount of sulphur precursor (CSPTMS) ranged from 10% to 20% of total silicon moles ($X = 0$ and 0.0041 for sample 2 and 3, respectively). Arenesulfonic modified SBA-15 (S-4 sample) was also synthesized using Brij76 as template (**C₁₈EO₁₀; Aldrich**). The molar composition of the mixture was similar to that used for the S-2 sample.

Other acid catalysts. Methanesulfonic acid (CH₃SO₃H), *p*-toluenesulfonic acid (C₇H₇SO₃H), Amberlyst-15 and H₃PW₁₂O₄₀ hydrate (HPA) were supplied by Aldrich. Arenesulfonic and propylsulfonic functionalized silica materials were acquired from Silicycle. SBA-15 supported HPA catalyst (HPA-SBA-15) was prepared by impregnating pure silica SBA-15 material (2 g; S_{BET}, 752 m²/g) with an organic solution of 3 g of HPA in 60 ml of methanol. The suspension was kept under stirring overnight at room temperature followed by drying of the impregnated catalyst using a rotatory evaporator and thermal treatment at 150 °C under vacuum.

2.2 Catalyst characterization.

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics TRISTAR 3000 system. The data were analysed using the BJH model and the pore volume (V_p) was taken at P/P₀= 0.975 single point. X-ray powder diffraction (XRD) data were acquired on a PHILIPS X`PERT diffractometer using Cu K α radiation. The data were recorded from 0.6 to 5° (2 θ) with a 0.02° resolution. Ion-exchange capacities of the sulfonic mesoporous materials were determined using aqueous solutions of sodium chloride (NaCl, 2M) as exchange agent. In a typical experiment, 0.05g of solid was added to 15 g of aqueous solution containing the salt.

The resulting suspension was allowed to equilibrate and thereafter titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). Sulphur and organic content was determined by means of elemental analysis (**HCNS**) in a Vario EL III apparatus and thermogravimetric analysis (SDT 2960 Simultaneous DSC-TGA, from TA Instruments). Tungsten content in the HPA-SBA-15 catalyst was determined by atomic emission spectroscopy with induced coupled plasma (ICP-AES) collected with a Varian Vista AX system. Table 1 and 2 summarizes the main physicochemical properties of all the catalysts.

2.3 Reaction procedure

The rearrangement of phenyl acetate was carried out in liquid phase at 100-170 °C in a stirred teflon-lined stainless-steel autoclave under autogenous pressure (with an initial nitrogen pressure of 4 bar in **order to increase the boiling point of reagents and thus insuring liquid phase at reaction temperature**). Reaction temperature was controlled using a thermometer immersed into the reactant mixture. To monitor the reaction, samples were withdrawn periodically for time intervals ranging from 0 to 24 hours. Typically, the total weight of the reaction mixture was 40.0 g : (40 – A – B) g of PAc : A g of solvent (dichloromethane, nitrobenzene, toluene) fixed to 0.0 g for solventless conditions or 20 g in presence of solvent : B g of phenol (B ranging from 0 g to 20 g). Catalyst loading was fixed in 0.5 g for solventless conditions and 0.25 g in presence of solvent. Reaction samples were analyzed by GC (Varian 3900 chromatograph) using a CP-SIL 8 CB column (30m x 0,25 mm, DF=0,25) and a FID detector. Sulfolane was chosen as internal standard for the GC analysis.

Selected reaction conditions yield low absolute conversion of PAc. Since the accuracy of the GC analysis for measurement of PAc absolute conversion and phenol

formation is questionable under the reaction conditions, catalytic results in the present work are presented in terms of yield towards HAP's compounds ($Y_{\text{HAP's}}$) which are the valuable reaction products, and in some instance **as production per acid site (PAS_{HAP's})**.

$$Y_{\text{HAP's}} = \frac{\text{mmols of produced HAP's}}{\text{mmols of fed PAc}} \times 100$$

$$\text{PAS}_{\text{HAP's}} = \frac{\text{mmols of produced HAP's}}{\text{mmols of acid sites}}$$

Product distribution has been normalised for the three compounds measured by GC analysis (2-HAP, 4-HAP and 4-AXAP). Phenol is also formed during the reaction but the presence of an initial high amount in the catalytic runs and the low PAc conversion make GC analysis inaccurate for determination of phenol yield. Additionally, heavy compounds formed by polymerization reactions and retained in the porous structured have not been quantified. Note that product distribution as defined in this work allows basically checking the *p*-selectivity of the catalysts.

Table 1. Physicochemical and textural properties of sulfonic-modified mesoporous materials.

Sample	Textural properties				Acid capacity and organic incorporation				
	d_{100} ^a (Å)	D_p ^b (Å)	S_{BET} (m ² /g)	V_p ^c (cm ³ /g)	Wall Thickness ^d (Å)	Acid Capacity ^e	Sulphur content ^f	Acid sites accessibility (%) ^g	Sulphur incorporation (%) ^h
S-1	97	82	666	1.23	30	1.58	1.52	100	91
S-2	101.6	80	720	0.93	37	1.71	1.66	100	99
S-3	103.1	76	733	0.81	43	2.87	2.87	100	86
S-4	61.4	43	828	0.98	28	1.34	1.51	89	90

^a $d(100)$ spacing.

^b Pore size from adsorption branch applying the BJH model.

^c The pore volume was taken at $P/P_0 = 0.975$ single point.

^d Calculated by a_o -pore size ($a_o = 2 d(100) / \sqrt{3}$).

^e Measured by titration using NaCl 2N as ionic exchanger and defined as mmol of H⁺ per g of SiO₂.

^f Sulphur content as mmol of S per g of SiO₂ calculated from HCNS and TGA analysis.

^g Defined as acid sites measured by titration / sulphur content from HCNS and TGA analysis * 100.

^h Defined as sulphur content from HCNS and TGA analysis / expected sulphur content at 100 % of incorporation of silica species* 100.

Table 2. Physicochemical and textural properties of other acid catalysts

Catalyst	S _{BET} (m ² /g)	Acid capacity ^a	W (wt. %)
Methanesulfonic acid	-	10.4	-
<i>p</i> -toluenesulfonic acid	-	5.3	-
Pr-SO ₃ H-SiO ₂	301	1.0	-
Ar-SO ₃ H-SiO ₂	279	0.8	-
Amberlyst-15	45	4.8	-
HPA	5	-	76.6
HPA-SBA-15	264	-	33 ^b

^a mmol of H⁺ per g of catalyst^b W content in the catalyst from ICP-AES analysis

3. Results and discussion

3.1 Fries rearrangement of phenyl acetate over sulfonic modified SBA-15 materials

A series of catalytic runs has been performed to assess the influence of the main variables involved in Fries rearrangement of phenyl acetate over sulfonic modified SBA-15 materials. Thus, catalyst properties such as pore size, nature and concentration of sulfonic sites and different reaction conditions (temperature, solvent and reagents initial ratios) have been tested. The main purpose of this study has been the selection of the optimal conditions to selectively produce HAP's compounds over sulfonic modified mesostructured SBA-15 materials.

Fries rearrangement experiments were carried out with a high concentration of PAc and in presence of phenol. The presence of the latter drives the mechanism towards the formation of 4-hydroxyacetophenone (reaction 3; scheme 1) and limits the formation of secondary products such as ketenes by equilibrium shift (reaction 5; scheme 1). Although the presence of high amounts of PAc promotes its autoacylation to yield 4-AXAP (reaction 2; scheme 1), an undesired product, 4-AXAP undergoes a dissociation to form 4-HAP (reaction 4; scheme 1), increasing the production of the *p*-hydroxyacetophenone.

Catalytic performance of different sulfonic modified mesostructured materials is illustrated in Figure 1. Propylsulfonic modified SBA-15 (S-1, sample) displays a very low activity in contrast with arenesulfonic functionalized samples (S-2 and S-3 samples), as already observed in other acid catalyzed reactions [24, 27-28]. The incorporation of a more electron withdrawing moiety (e.g. phenyl group) close to the sulfonic group increases significantly the acid strength of the material [23]. The increase of arenesulfonic groups loading (S-3 sample) leads to an enhancement of HAP's production. The catalytic activity of each arenesulfonic acid site in HAP's formation is also depicted in **Figure 1.a (right top)**. It can be seen that the production of HAP's per acid site increase slightly with the acid loading which may be due to a cooperation effect between proximal sulfonic groups as a consequence of the increased concentration of active acid sites in the catalyst [28]. Likewise, these catalytic results demonstrate the high accessibility of acid centres for these arenesulfonic modified mesostructured materials even with acid capacities close to 2.9 mmol H⁺ per g of silica. Lowering of the pore size (S-4 sample) does not change appreciably the HAP's production obtaining similar values to those obtained with S-2 sample.

Figure 1 b. illustrates the normalized product distribution (HAP's and 4-AXAP) after 4 hours of reaction. High 4-HAP/2-HAP molar ratio is preferred for paracetamol production, although in other applications low 4-HAP/2-HAP molar ratio may be required [29-30]. Arenesulfonic SBA-15 samples yield higher *p*-selectivity than that observed in propylsulfonic SBA-15. The different selectivity of alkylsulfonic and arenesulfonic containing SBA-15 materials, clearly evidenced in this work, has been also observed for other authors in the synthesis of Bisphenol-A [28]. Interestingly, the yield towards the different reaction products does not change with an increased number of acid sites. Likewise, selectivity towards the *p*-isomer is not improved with lower pore

size. Reacting molecules and/or intermediates appear not to be voluminous enough to undergo shape selectivity on this modified arenesulfonic catalysts. Nevertheless, this modified material could find application in other acid catalysed processes where reagents or products are bulkier.

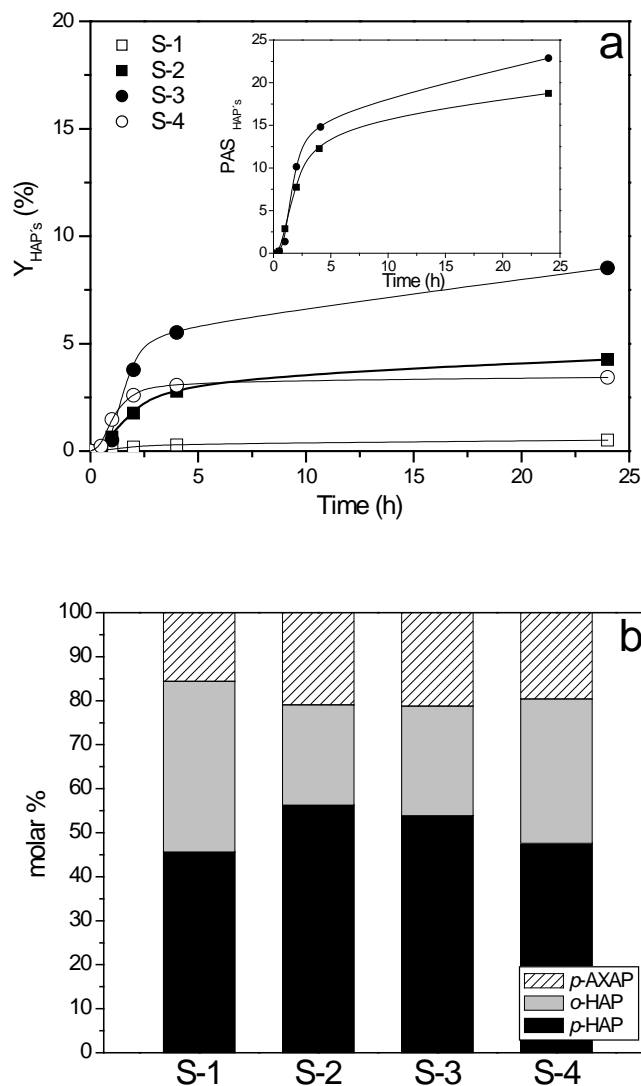


Figure 1. Production of HAP's over sulfonic SBA-15 with different pore size and acid content in solventless conditions. Reaction conditions: Temperature 150 °C; 30 g of PAC; Pac/Phenol mass ratio of 3; 0.5 g of catalyst. a) Activity and b) Normalized molar products distribution after 4 hours of reaction.

There is an evidence of catalyst deactivation for arenesulfonic modified SBA-15 samples after 4 hours of reaction. Leaching of arenesulfonic acid groups in the catalytic reaction using S-2 sample was examined. Elemental analysis revealed that sulphur

content was kept constant after the catalytic reaction at 150 °C for 24 h. However, organic content increased from 0.4 to 3.7 organic grams per g of SiO₂ for the catalyst after reaction. These analyses indicate that the decrease of conversion rate after 4 hours of reaction cannot be attributed to the leaching of active sites, but it is mainly due to the catalysts poisoning by strong organic adsorption. These results should be related to analogue deactivation mechanism observed for zeolites, assigned to the irreversible adsorption of higher molecular weight compounds formed via ketene polymerization (reaction 6, scheme 1). These bulky compounds are difficult to extract and generate permanent deactivation [31]. TG analyses of fresh and used S-2 sample shown in Figure 2 confirm the elemental analysis. Fresh catalysts show a clear desorption peak for temperatures over 400 °C attributed to the decomposition of arenesulfonic groups. Catalyst after 4 hours of reaction shows a clear retention of a great amount of organic species within the pores (region I in Figure 2, b), which is attributed to adsorption of phenolic compounds and other low-temperature boiling point species. Likewise, an important loss of weight at high temperatures is observed for used catalyst in contrast with the fresh one (region III in Figure 2, b). These strongly-adsorbed organic species might be probably interacting with acid sites and being the main responsible for catalyst deactivation. The development of efficient regeneration methods will therefore be necessary if these materials are considered for practical applications.

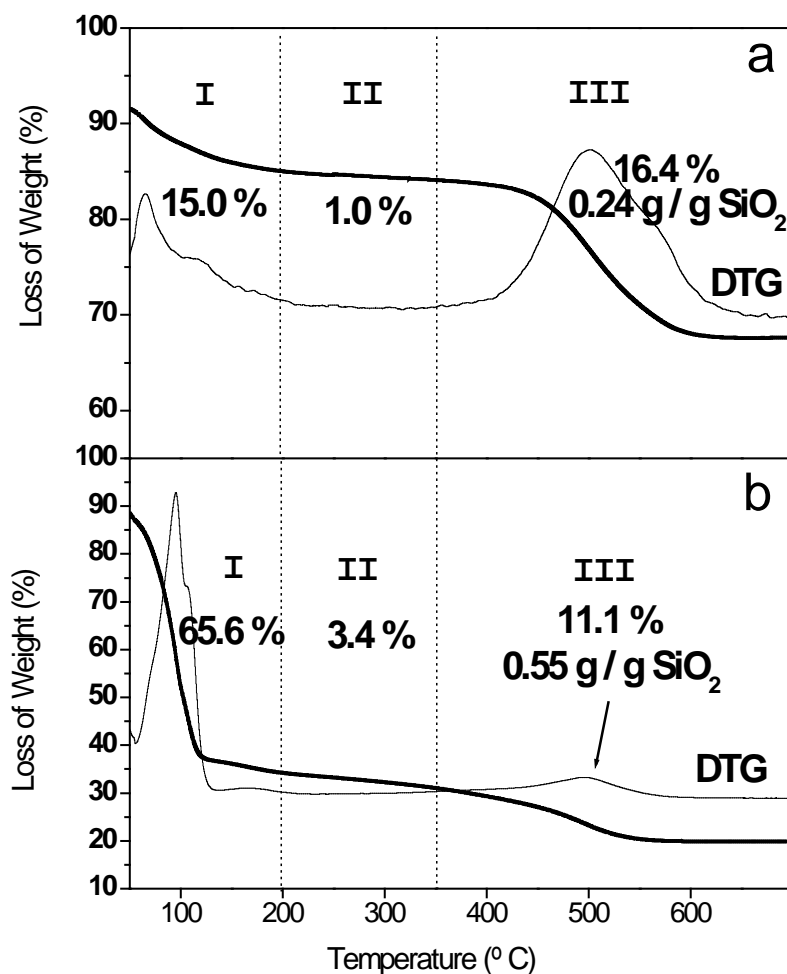


Figure 2. Thermogravimetric analysis (loss of weight during thermal treatment and its derivative, DTG) for (a) fresh catalyst and (b) after reaction. Temperature 150 °C; 30 g of PAc; PAc/Phenol mass ratio of 3; No solvent; 0.5 g of S-2 catalyst.

From the above mentioned results, arenesulfonic modified SBA-15 mesostructured material seems to be an interesting catalyst for the liquid phase Fries rearrangement of phenyl acetate. With the purpose of optimising activity and selectivity performance of this catalyst, in the following discussion we will show the influence of phenol to PAc mass ratio, the presence of solvent and temperature.

3.1.1 Influence of the phenol / phenyl acetate starting mass ratio.

Different catalytic tests have been carried out in order to establish the influence of different amounts of phenol in the reaction medium at 150 °C over arenesulfonic SBA-

15 (Sample 2, Table 1). Figure 3 a. depicts the activity of each reaction in terms of yield towards HAP's isomers and Figure 3 b. shows the normalized molar products distribution after 4 hours of reaction.

The production of HAP's is clearly enhanced when a PAc / phenol mass starting ratio of 3 is used. When no phenol is added, the production suffers a significant decrease accompanied with a low selectivity towards 4-HAP isomer. These facts are in agreement with the above-reported mechanism [3], wherein the presence of phenol is an essential condition to favour the production of 4-HAP (reaction 3; scheme 1) and to inhibit the formation of ketenes by PAc dissociation (reaction 5; scheme 1). Note that in absence of phenol, the presence of 4-HAP is coming from the phenol originated in PAc dissociation (reaction 5; scheme 1) and therefore the production is slower. However, a major increase of phenol up to PAc/phenol mass ratio of 1 does not change appreciably HAP's production. The access of phenyl acetate to the internal acid sites is partially restricted by the filling of catalyst pore system preferentially with phenol when a high amount of the latter is present in the reaction medium. Interestingly, the presence of a high concentration of phenol seems to delay catalyst deactivation as a consequence of the inhibition of ketene formation (reaction 5; scheme 1).

The phenol concentration in the reaction medium induces significant changes in the product distribution as illustrated in Figure 3 b. A gradual decrease of PAc/phenol mass starting ratio, i.e. introducing more phenol in the system, results in increased 4-HAP selectivity according to reaction numbered as 3 in scheme 1. However PAc/Phenol mass starting ratio below 3 did not favoured further the p-isomer selectivity in these conditions. As expected the autoacylation of PAc towards 4-AXAP (reaction 2, scheme 1) is clearly favoured with the progressive increase of the former in the reaction medium.

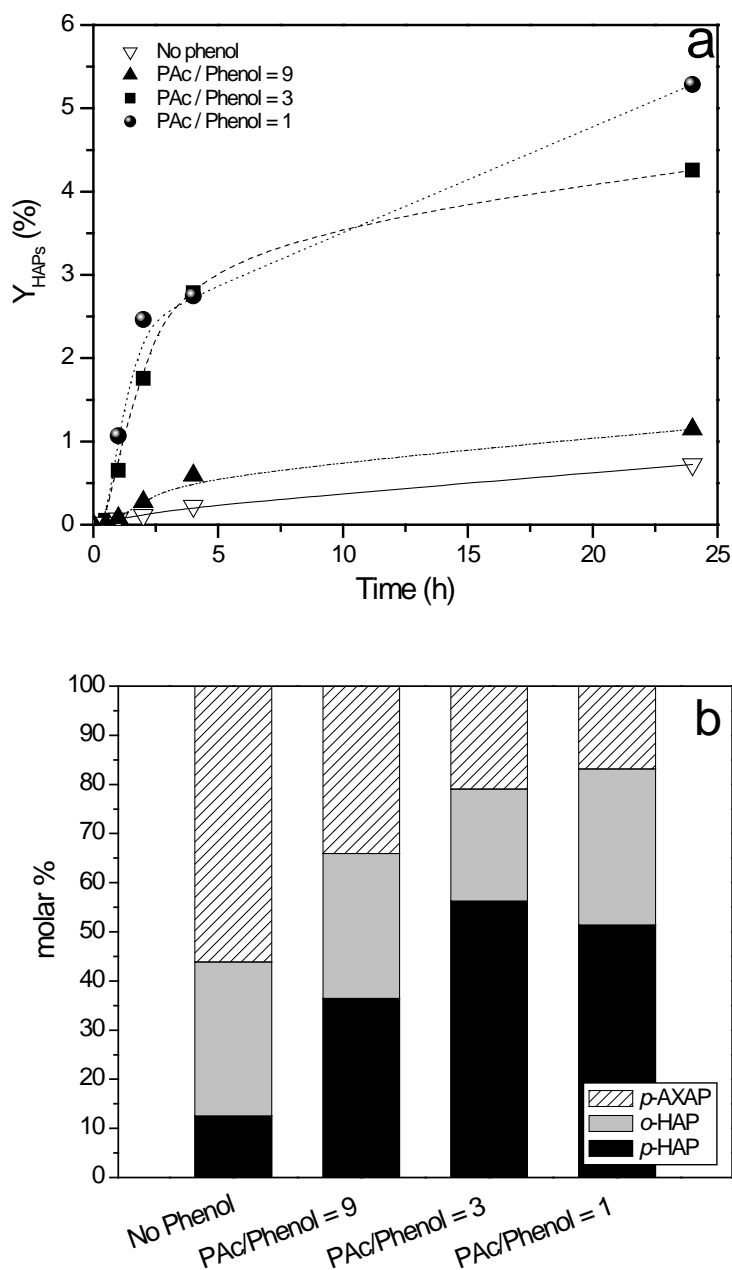


Figure 3. Production of HAP's over arenesulfonic SBA-15 catalyst with different amount of phenol in the reaction medium and solventless conditions. Reaction conditions: Temperature 150°C; 0.5 g of catalyst. a) Activity and b) Normalized molar products distribution after 4 hours of reaction.

In conclusion, initial incorporation of phenol significantly improves the production and the *p*-selectivity. This improvement reaches a maximum at the PAc/phenol mass starting ratio of 3.

3.1.2 Influence of the temperature.

Several catalytic runs have been carried out with the purpose of determining the influence of the temperature in the Fries rearrangement of phenyl acetate over arenesulfonic SBA-15 (Sample 2, Table 1) with a PAC/phenol starting mass ratio of 3 and solventless conditions. Temperatures between 100°C and 170°C are usually reported in literature for liquid phase Fries rearrangement. Figure 4 a. depicts the activity of each test in terms of yield on HAP's isomers.

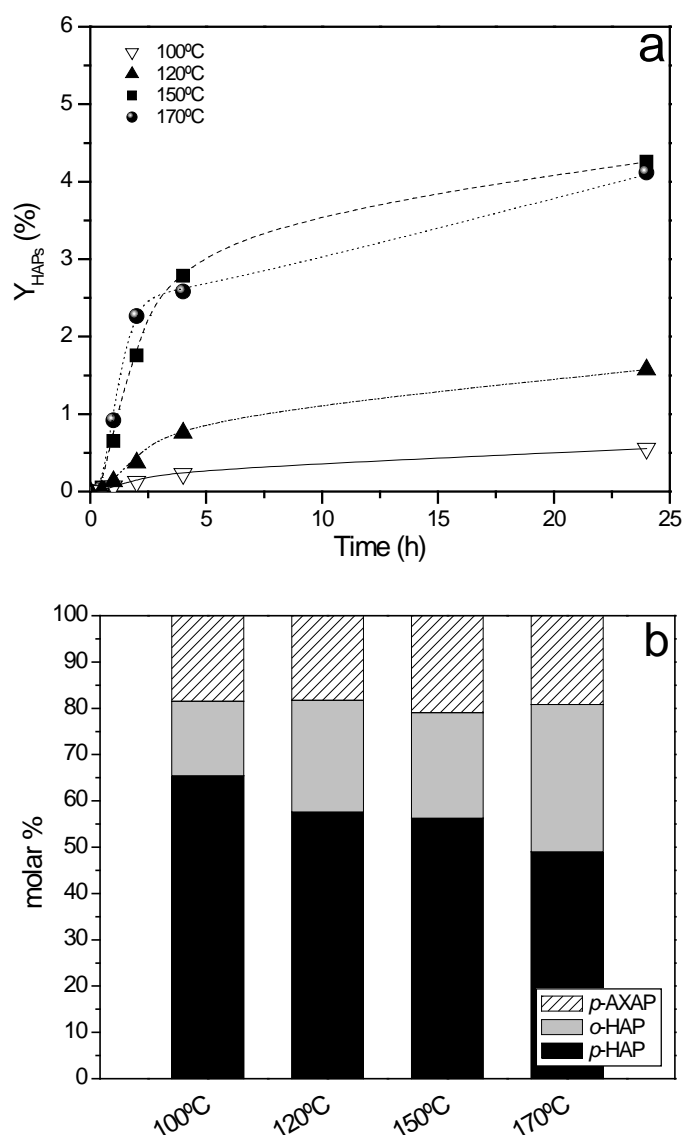


Figure 4. Production of HAP's over arenesulfonic SBA-15 catalyst at different reaction temperatures in solventless conditions. Reaction conditions: 30 g of PAC; PAC/Phenol mass ratio of 3; 0.5 g of catalyst. a) Activity and b) Normalized molar products distribution after 4 hours of reaction.

Production of HAP's increases with the temperature up to 150°C. Higher increase of the temperature (170°C) does not further improve the production of HAP's probably due to a faster deactivation process enhanced by higher temperature. Figure 4 b. shows the product molar distribution after 4 hours of reaction. The gradual increase of the temperature leads to a drop in the amount of 4-HAP isomer with respect to the 2-HAP.

3.1.3 Influence of the solvent.

Different catalytic tests have been accomplished to evaluate the possibility of using solvents in order not only to upgrade catalyst performance, but also to reduce or even avoid its loss of activity. The catalytic runs were carried out over modified arenesulfonic SBA-15 (Sample 2, Table 1) at 150°C and with a PAc/phenol starting mass ratio of 3. Conventional solvents usually used for the liquid Fries rearrangement of phenyl acetate such as toluene, nitrobenzene and dichloromethane have been selected [3]. Figure 5 a. depicts the activity in terms of yield on HAP's isomers and Figure 5 b. illustrates the products molar distribution after 4 hours of reaction. Reaction without solvent is also included for comparison. The low polarity of toluene (dielectric constant 2.4) could be the reason of the low production rates achieved with this solvent. It does not present affinity for the highly polar reaction compounds and therefore global diffusion of species is hindered. Recently, nitrobenzene has been used as solvent (dielectric constant 35.0) in Fries rearrangement over heteropoly acid catalyst with acceptable results [12]. However, when used in heterogeneous Fries rearrangement over arenesulfonic SBA-15, it has displayed no improvement either in productivity or in regards to deactivation. The high polar solvent competes with the diffusion of the reagents (PAc and phenol) within the mesopore structure. Surprisingly, the use of dichloromethane as solvent with dielectric constant (8.9) similar to that of PAc and

phenol (6.9 and 9.8, respectively) exhibits the highest production rates as compared to other solvents and better than in absence of solvent. **After 24 hours of reaction the absolute PAc conversion increased up to that means a HAP's selectivity of ca.**

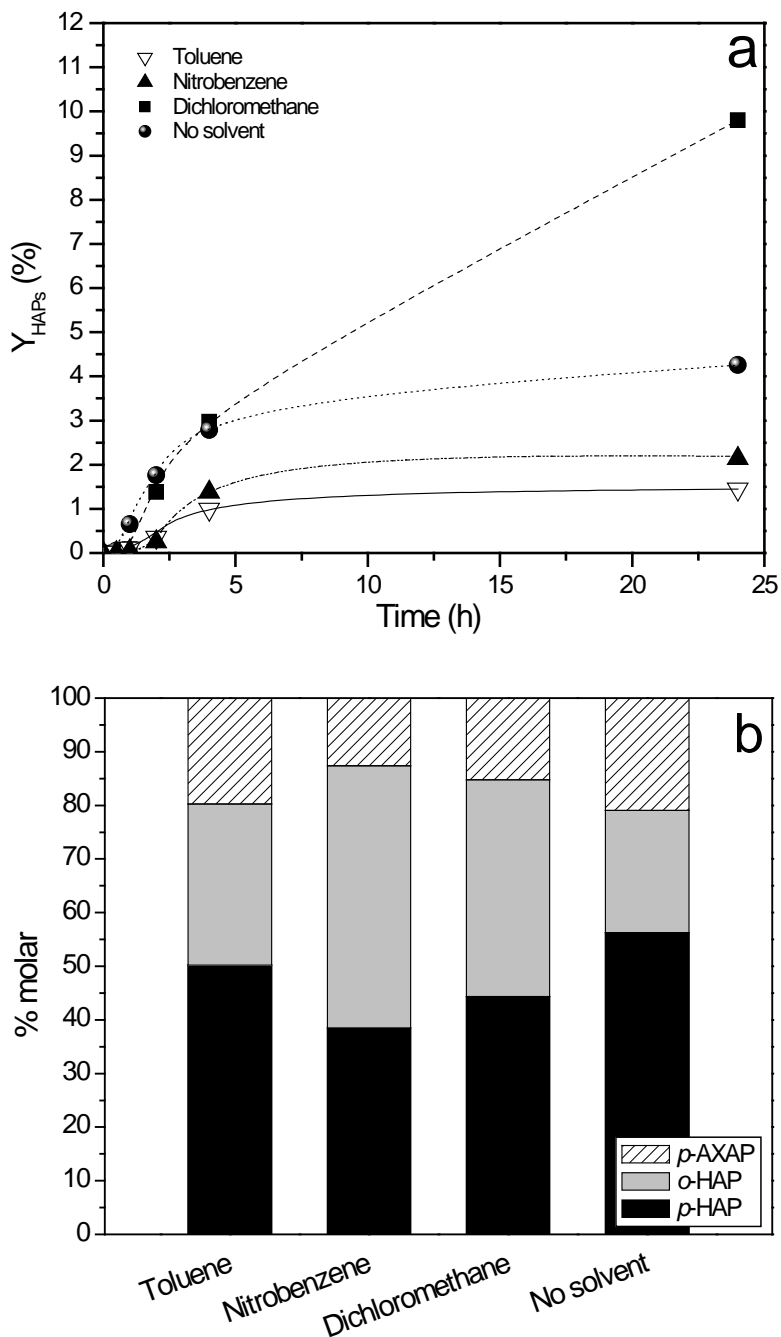


Figure 5. Production of HAP's over arenesulfonic SBA-15 with different solvents. Reaction conditions: Temperature 150 °C; PAc/catalyst mass ratio of 60; PAc/Phenol mass ratio of 3; 20 g of solvent. a) Activity and b) Normalized molar products distribution after 4 hours of reaction.

In terms of catalytic deactivation, the presence of toluene and nitrobenzene did not avoid the deactivation of the catalysts after 4 hours of reaction. In contrast, the production of HAP's isomers (and 4-AXAP) still goes on after 24 h of reaction when dichloromethane is used as solvent. As it has been commented above, the origin of deactivation is assigned to the irreversible adsorption of higher molecular weight compounds formed via ketene polymerization (reaction 6, scheme 1) which are difficult to extract and generate permanent deactivation [31]. According to our catalytic results the presence of dichloromethane could inhibit the formation of bulky compounds or extract them from the active sites. The use of this solvent over arenesulfonic modified SBA-15 is an attractive alternative in order to avoid serious problems associated with catalyst deactivation for this particular reaction.

With regard to products distribution, the use of solvents yields a decrease in the formation of *p*-isomer respect to the 2-HAP, mainly for polar solvents such as nitrobenzene and dichloromethane.

3.2 Fries rearrangement of phenyl acetate over different acid solid catalysts

Catalytic performance of arenesulfonic modified SBA-15 samples (S-3 sample) has been compared with other sulfonic functionalized catalysts such as Amberlyst-15 sulfonic resin, sulfonic silica-supported materials and two homogeneous catalytic systems, methanesulfonic and *p*-toluenesulfonic acids. In order to obtain a quantitative comparison of the catalytic performance of the different sulfonated catalysts, the specific production of HAP's isomers per mmol of acid site has been evaluated and monitored with the course of the reaction (Figure 6 a.).

Arenesulfonic SBA-15 catalyst (S-3 sample) displays the highest performance reaching a maximum value of 22.8 mmol of produced HAP's per acid site after 24

hours, almost four times the production obtained with Amberlyst 15. The apparently limited catalytic behaviour displayed by the sulfonic resin can be explained in terms of the lower accessibility of the sulfonic centres as well as the possible thermal degradation of its structure.

The activity of S-3 sample has been also compared with sulfonic modified non-ordered silica materials. Pr-SO₃H-SiO₂ sample gives a low production of HAP's compounds as occurred with S-1 sample and confirming that propylsulfonic groups possess a limited acid strength to catalyze effectively this particular reaction. This effect is also observed with the homogeneous counterparts since the aromatic-activated *p*-toluenesulfonic acid is more active than the methanesulfonic acid. On the other hand, Ar-SO₃H-SiO₂ showed six times less activity per acid site than S-3 sample, though both possess similar arenesulfonic acid groups. It is clear that the mesoscopic ordering of S-3 sample favours the diffusion of reactant and products molecules in liquid phase rearrangement of phenylacetate.

Figure 6 b. illustrates the normalized product distribution (HAP's and 4-AXAP) after 4 hours of reaction. Amberlyst-15 and arenesulfonic SBA-15 samples yield the highest *p*-selectivity. Homogeneous methanesulfonic and *p*-toluenesulfonic acid catalysts present orthoselectivity instead of paraselectivity. Interestingly, the confinement of sulfonic group within a porous structure leads to an enhancement of *p*-selectivity. This fact could be related to the faster diffusion of phenol within the porous structure which would lead to a higher concentration in the solid phase than that existing in the liquid phase and hence promoting 4-HAP formation.

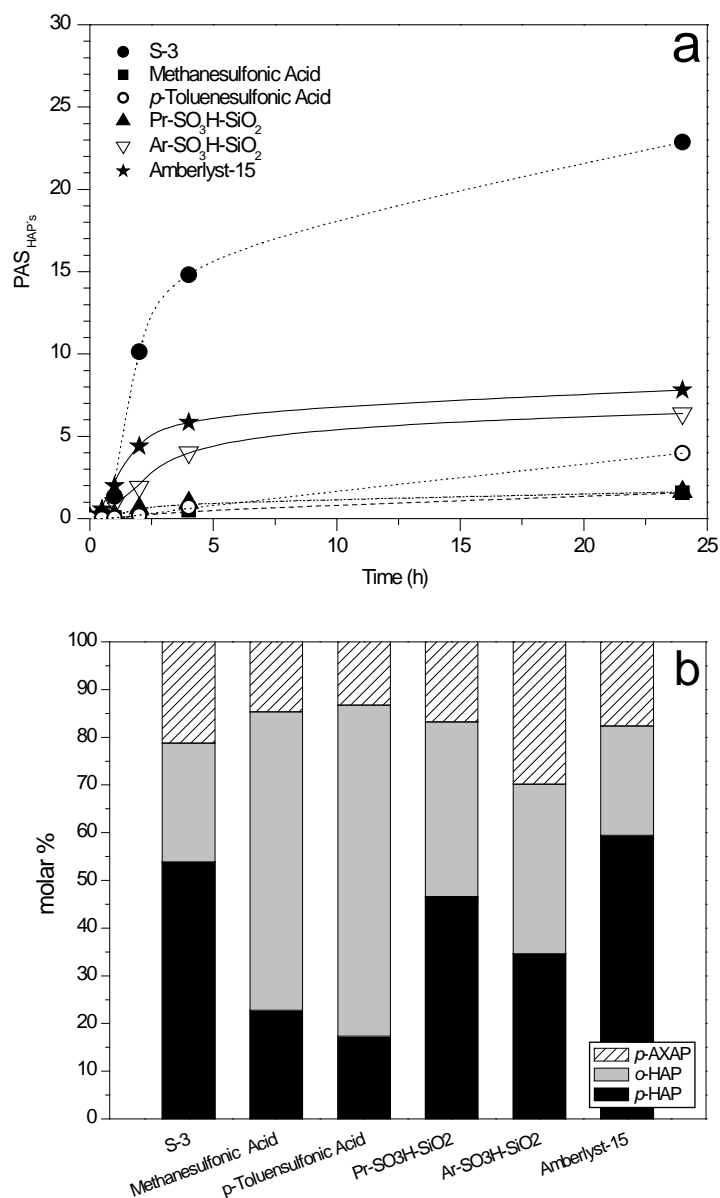


Figure 6. Production of HAP's over different sulfonated acid solid catalysts in solventless conditions. Reaction conditions: Temperature 150°C; 30 g of PAC; 0.5 g of catalyst; PAC/Phenol mass ratio of 3. a) Activity and b) Normalized molar products distribution after 4 hours of reaction.

Heteropoly acid H₃PW₁₂O₄₀ (HPA) supported on silica has been recently found as an active catalyst in the liquid phase rearrangement of phenylacetate [13]. We have considered interesting to compare the catalytic performance of HPA catalyst unsupported and supported on SBA-15 with the **arenesulfonic** modified SBA-15 catalyst (S-3 sample) under the same reaction conditions. Figure 7.a show the

production of HAP's for the three catalytic systems. It should be noted that HPA is readily soluble in PAc at elevated temperatures [12] therefore this case must be considered as homogeneous catalysis. Unsupported HPA gave a high initial production as compared with heterogeneous catalysts which must be attributed to the ease of access to the acid sites for the homogenous catalyst. Interestingly, S-3 sample showed similar production rate of HPA-SBA-15 catalyst and even reached comparable values to those obtained with the homogenous system after 24 hours of reaction.

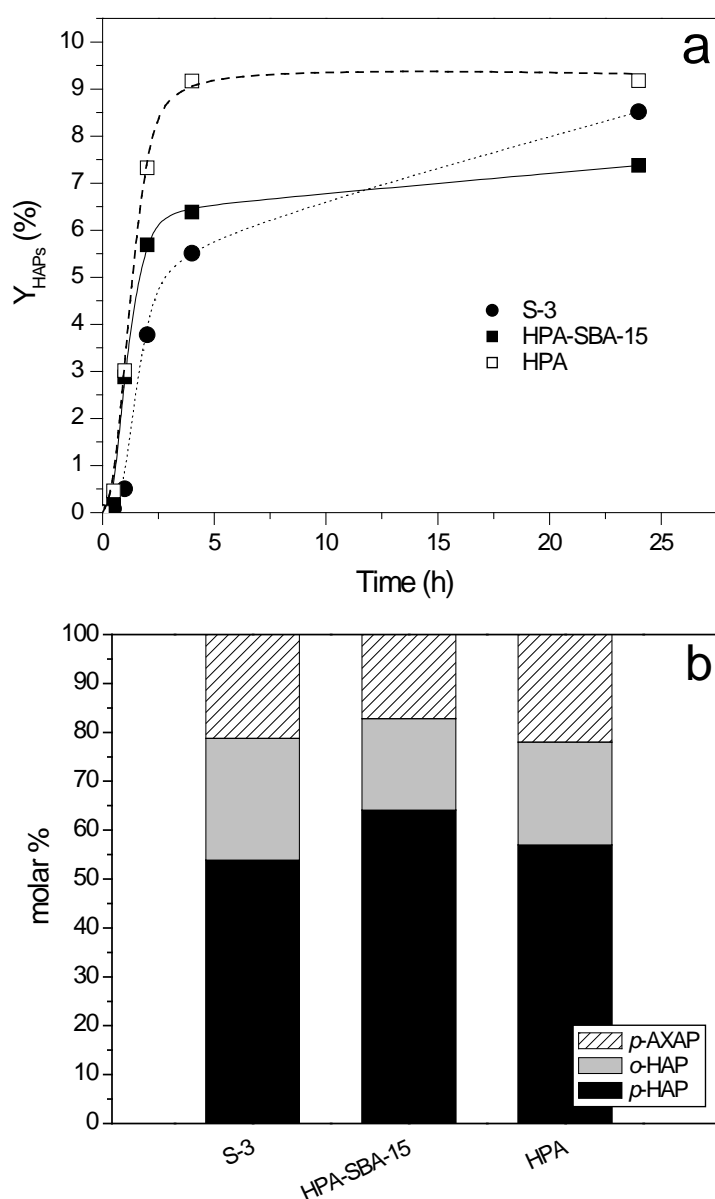


Figure 7. Production of HAP's over HPA acid solid catalysts in solventless conditions. Reaction conditions: Temperature 150°C; 30 g of PAc; 0.5 g of catalyst; PAc/Phenol mass ratio of 3. a) Activity and b) Normalized molar products distribution after 4 hours of reaction.

Conclusions

Arenesulfonic modified mesostructured SBA-15 is shown as an active catalyst in the liquid-phase Fries rearrangement of phenyl acetate. The arenesulfonic acid-centers show high catalytic performance as compared to other homogeneous and heterogeneous acid catalysts. This high activity is accompanied with a remarkable stability of sulphur species during the reaction. Reaction conditions have been optimized in order to increase production of the most desired products, the hydroxyacetophenones. After 4 hours of reaction catalytic activity is dramatically reduced due to catalyst deactivation. However, when dichloromethane is used as solvent over arenesulfonic modified SBA-15 material, an enhancement of HAP's production is clearly evidenced and more important with a slower catalyst deactivation. The use of dichloromethane for this particular reaction open a new field of research to be further explored with the purpose of obtaining higher yields on HAP's compounds. Additionally, the slow decay of activity in presence of dichloromethane may suggest an easy regeneration of the catalyst. Catalytic studies with dichloromethane as solvent over arenesulfonic materials for Fries rearrangement are already under investigation.

Acknowledgements

The authors thank the CICYT (PPQ2002-02382) and "Programa Grupos Estratégicos de la CAM" for the financial support.

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