

PERFLUORINATED NAFION-MODIFIED SBA-15 MATERIALS FOR CATALYTIC ACYLATION OF ANISOLE

F. Martínez, G. Morales, A. Martín and R. van Grieken*

Department of Chemical and Environmental Technology, ESCET,
Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain.

Published on:

Applied Catalysis A: General 347 (2008) 169-178

[doi:10.1016/j.apcata.2008.06.015](https://doi.org/10.1016/j.apcata.2008.06.015)

PERFLUORINATED NAFION-MODIFIED SBA-15 MATERIALS FOR CATALYTIC ACYLATION OF ANISOLE

F. Martínez, G. Morales, A. Martín and R. van Grieken*

Department of Chemical and Environmental Technology, ESCET,
Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain.

ABSTRACT

Mesoporous SBA-15 silica materials have been functionalized with perfluorosulfonic acidic Nafion resin using a post-synthetic impregnation method. The remarkable physicochemical properties of hexagonally ordered SBA-15 silicas (high surface area, large and narrow pore size distribution and thermal stability) make them particularly attractive for the immobilization of strongly acidic perfluorosulfonic sites. The loading of Nafion resin was varied between 10 and 20 wt%. The synthesized Nafion/SBA-15 hybrid materials were evaluated in the Friedel Crafts acylation of anisole. The optimum catalytic performance of Nafion/SBA-15 hybrid material with a resin loading around 13 wt% was compared with other perfluorosulfonic acid-based catalysts either commercially available or prepared following recipes reported in the literature. The influence of several variables on the acylation of anisole, such as the reaction temperature and the anisole/acylating agent ratio, has also been assessed by means of a factorial design of experiments. The catalytic activity of Nafion-modified SBA-15 materials is strongly affected by the reaction temperature, whereas a lesser effect was evidenced for the reaction mixture composition in the range under study. The optimal operation conditions in terms of anisole conversion were achieved at 150°C and equimolar anisole/acetic anhydride mixture. The deposition of poly-acetylated by-products on the catalytic acid sites is mainly responsible for the catalyst deactivation, whereas the leaching of sulfonic groups and their contribution in the anisole acylation via homogeneous catalysis has been ruled out. Finally, the recovery of the catalytic activity by regeneration of the spent catalyst by refluxing in nitric acid solution was demonstrated. The characterization of the regenerated catalyst indicates that the regained activity is likely related to the displacement of the deactivating by-products out of the perfluorosulfonic acid sites during the nitric acid regeneration.

Keywords: mesostructured silica, SBA-15, Nafion, anisole, acylation.

*To whom correspondence should be addressed

e-mail: rafael.vangrieken@urjc.es

Tel.: +34 91 665 50 72 Fax: +34 91 488 70 68

1. Introduction

Manufacturing processes for the production of high added-value fine chemicals, based on acylation, rearrangement, isomerization or esterification reactions, are currently carried out by homogeneous Lewis acids (e.g. AlCl_3 , BF_3) or Brønsted acids (strong mineral acids such as H_2SO_4 , HF) [1]. However, the use of corrosive mineral acids or Lewis-acid catalysts presents inevitable limitations in terms of non-reusability and non-desirable toxicity, being the latter of special attention by the increasingly stringent environmental regulations [2]. Most of these problems can be overcome by the application of acid-functionalized solid catalysts, but they must show a catalytic activity at least comparable to their homogeneous counterparts. In this sense, the efficiency of heterogeneous catalysts can be significantly improved by enhancing the strength of the supported acid sites, leading to solid acid catalysts capable to be considered as a potential alternative for conventional homogeneous catalytic systems. Thus, the application of zeolites has been an active area of research [3-4], but the low range of available pore sizes (< 1 nm) is considered an important drawback. The synthesis of Al-MCM-41 constituted a remarkable achievement in this field since the pore size could be extended up to 10 nm. Although it is applicable to reactions involving large reactants and products, multiple examples that evidence the limitation of the lower acid strength of aluminum sites have been reported [5]. In a different approach, sulfonic acid groups supported on porous silicas have been widely studied [6]. They provide an alternative way of endowing surface acidity to mesoporous molecular sieves, such as MCM-41 [7-8], HMS [9], and SBA-15 [10] materials, in contrast to solid Lewis-acid catalysts that rely on the isomorphous substitution of the silicon atoms by aluminium atoms [11-12]. Silica-supported sulfonic acids are usually synthesised either via co-condensation during silica gel formation or through post-synthesis grafting on the silica walls, always using a suitable sulfur-containing silane. Unlike Amberlyst-type resins based on acid-functionalized polystyrene polymers and characterized by high concentrations of

sulfonic acid groups, sulfonic acid-modified silicas usually result in lower acid capacities, regardless of the synthetic procedure employed. However, the nature of the anchored organic species can be manipulated to control the sulfonic acid strength [13]. In the case of sulfonic acid modified-SBA-15 mesoporous materials, arenesulfonic groups have resulted more effective than propylsulfonic groups in several acid-catalyzed reactions, and they have also been more active than conventional homogeneous systems [6, 14].

Nafion-perfluorosulfonic acid resin, developed by copolymerization of a perfluorosulfonyl ether co-monomer and tetrafluoroethylene, is presented as a superacid solid as a consequence of the fluorine atoms near the sulfonic acid groups [15-18]. As it was stated by means of ammonia adsorption calorimetry, the acid strength of its active sites is considerably superior to that of other sulfonic acid moieties on polymeric and silica supports (alkyl- and aryl-sulfonic sites) [19]. Nafion resin itself has been tested in several acid-catalyzed reactions [20-21]. However, the catalytic performance of these materials is normally limited by restricted surface area and low availability of acid sites in the polymeric resin. To overcome these textural and steric constraints, silica-supported Nafion resin nanocomposites, such as the commercially available Nafion[®]-SAC-13, have been developed and tested for evaluation in several acid-catalyzed reactions [22]. The impregnation of Nafion resin in silica has provided perfluorosulfonic acid materials with higher surface areas and more density of available acid sites leading to the enhancement of their acid catalytic properties [23]. Wang and Guin also reported the incorporation of Nafion to mesoporous MCM-41 silica by sol-gel techniques, concluding that the use of impregnation is more beneficial than the sol-gel technique for the etherification of olefins [24]. Likewise, several publications have dealt with the immobilization of perfluorosulfonic acid silanes by post-synthetic grafting strategies [25-26] or direct one-step synthesis [27] over ordered mesoporous silicas searching for acid strengths comparable to that shown by perfluorinated sulfonic acid Nafion resins. However, the limited availability of suitable fluorinated silanes hinders the applicability of this kind of materials for the production in large scale. In this work, a simple impregnation method for the preparation of highly acidic Nafion-based catalyst over a mesoporous SBA-15 silica matrix is studied. This silica support provides a high surface area with a narrow pore size distribution within the mesoscopic scale that make feasible the access of bulky substrates, as well as a remarkable stability due to the thick

silica walls that constitute the framework channels [28]. The activity of acidic hybrid organic-inorganic Nafion SBA-15 materials has been evaluated on the anisole acylation with acetic anhydride for the production of methoxyacetophenones, which are key intermediates for the preparation of several pharmaceuticals and fragrances [2]. The influence of the acetic anhydride to anisole ratio and the reaction temperature were studied by means of a factorial design of experiments. Likewise, the activity, stability and reusability of these materials have been compared with other known heterogeneous acid catalysts with similar acid strengths.

2. Experimental Section

2.1 Catalysts preparation

Ordered mesoporous SBA-15 silica was synthesized according to well established method described elsewhere [28]. In a typical synthesis, 4 g of the structure-directing agent - block-copolymer Pluronic 123 (EO₂₀PO₇₀EO₂₀, Mn 5800, Aldrich) - were dissolved with stirring in 1.9 M HCl (125 mL) at room temperature. The resultant micellar solution was then heated to 40°C before adding the silica source, tetraethylorthosilicate (TEOS; Aldrich). After being stirred for 20 h at 40 °C, the mixture was aged under static conditions and autogeneous pressure at 100 °C for 24 h. Thereafter, the solid product was recovered by filtration and air dried overnight. The templating surfactant was removed by calcination at 550°C for 5 h (1.8 °C/min heating ramp). The incorporation of the perfluorosulfonic Nafion resin was carried out by a simple impregnation procedure using a Nafion 5 wt% alcoholic solution as precursor (Aldrich) [24]. This impregnation method consisted in the dispersion of powder SBA-15 silica with the appropriate amount of Nafion alcoholic solution to achieve theoretical 10, 15, and 20 weight percentages of resin loading. Thus, the resultant hybrid materials were denoted as Nafion(X)/SBA-15, being X 10, 15, or 20. The impregnation process was carried out at 60°C and atmospheric pressure under vigorous stirring for 2 hours. Finally, the complete removal of solvent was accomplished by evaporation at room temperature for 24 hours in static conditions.

Nafion[®]/silica composite SAC-13 with resin content in the range of 10-20 wt % was supplied by Aldrich. The hybrid organic-inorganic SBA-15 silica functionalized with perfluoroalkylsulfonic acid groups (herein denoted as SFS) was prepared adapting the

procedure described by Corma et al [26]: 2 g of SBA-15 silica were dried at 120°C for 8 hours and functionalized with 1 g of the perfluorinated precursor 1,2,2-trifluoro-2-hydroxi-1-trifluoro-methylethane sulfonic acid sultone (FluoroChem) in 50 mL of dry toluene under nitrogen atmosphere. This precursor reacts with the surface silanol groups of the mesoporous silica and forms a covalently bonded perfluorosulfonic moiety. The solid product is vacuum-filtered, washed thoroughly with toluene and finally dried at 100°C overnight.

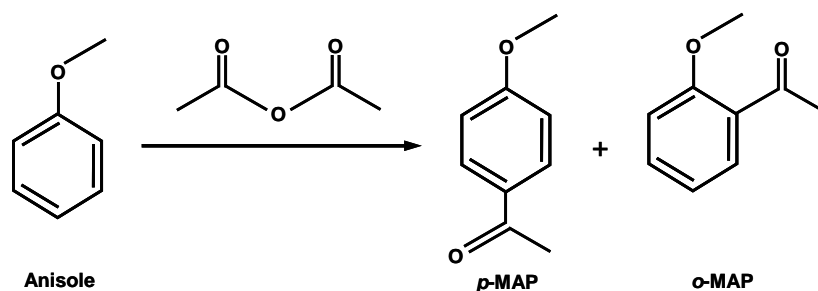
2.2 Catalyst characterization.

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics TRISTAR 3000 system. The data were analyzed using the BJH and BET models and the pore total volume (V_p) was assigned at $P/P_0 = 0.975$ as single point. The t-plot method was applied to calculate the micropore volume and mesoporous pore volumes. X-ray powder diffraction (XRD) patterns were acquired on a PHILIPS X'PERT diffractometer using Cu $K\alpha$ radiation. The data were recorded from 0.6 to 5° (2θ) with a resolution of 0.02°. Transmission electron microscopy (TEM) microphotographs and energy-dispersive X-ray (EDX) microanalyses were carried out on a PHILIPS TECNAI-20 electronic microscope operating at 200 kV. Cation-exchange capacities corresponding to the perfluorosulfonic acid-modified mesostructured materials were determined using saturated solutions of NaCl in ethanol as cationic-exchange agent. In a typical experiment, 0.05g of solid was added to 15g of alcoholic solution containing the sodium salt. The resulting suspension was allowed to equilibrate and thereafter it was titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). Sulfur and total organic content were determined by means of Elemental Analysis (HCNS) in a Vario EL III apparatus and thermogravimetric analysis in a SDT 2960 simultaneous DSC-TGA from TA Instruments (5°Cmin⁻¹ ramp until 700°C in air atmosphere), respectively.

2.3 Reaction procedure.

In order to check the catalytic performance of the perfluorosulfonic acid-modified mesostructured materials, a reaction demanding strong acid catalytic sites such as the acylation of anisole to form methoxyacetophenones (MAPs) was studied (Scheme 1). An second acid-catalyzed reaction such as the Fries rearrangement of phenyl acetate

was also tested for additional evaluation of the catalytic performance of the different perfluorosulfonic acid-based catalysts. All the catalytic experiments were carried out in a teflon-lined stainless steel stirred autoclave equipped with a temperature controller and a pressure gauge. Reactants and catalyst were charged at room temperature, the system was pressurised with nitrogen (4 bar) to ensure liquid phase of the reaction medium, and then heated using a thermally-controlled oven up to the reaction temperature. Stirring was fixed for all the experiments at 500 rpm to avoid diffusional limitations. Samples were withdrawn at selected reaction times ranging from 0 to 5 h. Reaction products were identified and quantified by gas chromatography, using a GC-3900 Varian chromatograph equipped with a CPSIL 8 CB capillary column (30 m x 0.25 mm, film thickness 0.25 μ m) and flame ionization detector (FID).



Scheme 1. Simplified reaction scheme for the acylation of anisole with acetic anhydride.

3. Results and Discussion

3.1 Synthesis of Nafion-modified mesostructured SBA-15 silica materials

Hybrid Nafion/SBA-15 silicas prepared by impregnation respond to the need of supporting strong acid catalysts over materials with extended surface area in order to provide well-dispersed active sites for application in acid-catalyzed reactions. Crucial points to ensure a homogeneous deposition of the perfluorosulfonic resin on the silica support are the Nafion concentration of the impregnating solution and the control of the solvent evaporation during the following drying step. Since the solvent is the ethanol accompanying the commercial Nafion resin, there was no need to regenerate the acid form of perfluorosulfonic acid sites once the impregnation process was completed. Pre-fixed Nafion contents were selected in order to provide the maximum acid capacity, preserving the textural properties of the SBA-15 silica support.

Nitrogen adsorption-desorption isotherms and XRD patterns of Nafion-modified materials and those corresponding to the pure siliceous SBA-15 analogues are illustrated in Figures 1a and 1b, respectively. XRD patterns of Nafion/SBA-15 samples evidence the presence of mesophases with hexagonal $p6mm$ symmetry, since the characteristic 100, 110 and 200 diffractions are clearly distinguished in all the materials. The polymer deposition over the mesoporous material for Nafion-impregnated samples provokes a relevant increase in the intensity of the (100) reflection observed for the two-dimensional (2D) hexagonal mesophase, while the reflections observed at higher angles do not show a similar trend. These XRD lines normally decrease in intensity as guest species are loaded in the mesopores, and such an intensity change can be used as a useful means of judging the location of the guest species. However, contrary to most cases, our Nafion/SBA-15 samples exhibit a significant increase in the diffraction intensity when Nafion resin is loaded within the porous structure. These XRD patterns could indicate that the process of impregnation results in an increase of the apparent density of the mesopore walls promoting the increase of the X-ray scattering contrast between the walls and the pores of the material as it has been reported in literature [29, 30]. Therefore, this suggests at least a partial incorporation of the Nafion polymer along the channel walls of the mesostructured silica support.

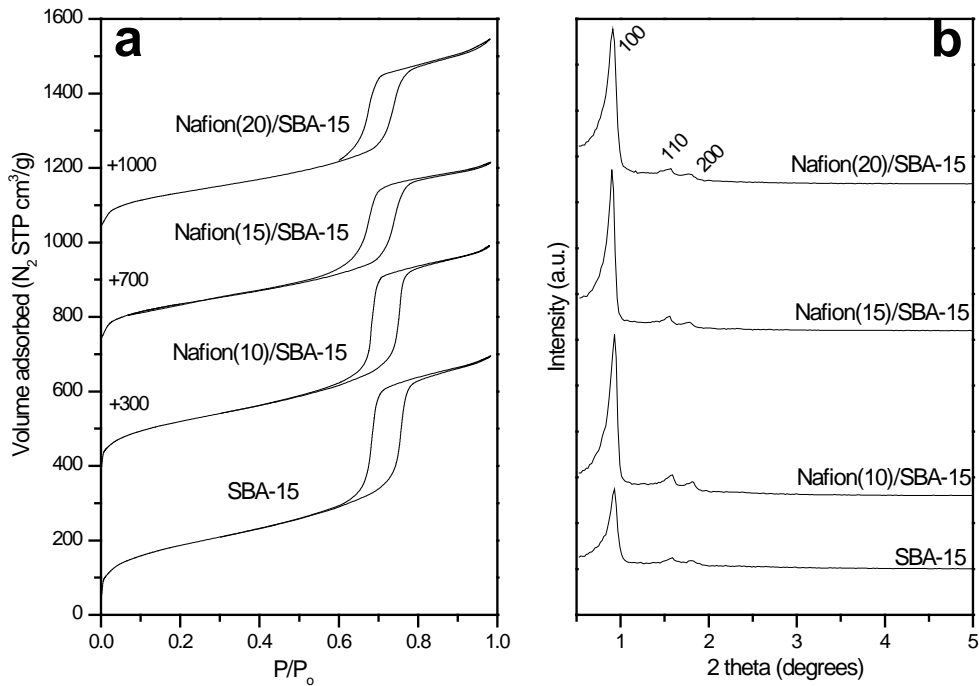


Figure 1. (a) Nitrogen adsorption isotherms at 77 K; and (b) X-ray diffraction patterns for Nafion-modified mesostructured materials.

Looking at the nitrogen isotherms, all the materials displayed typical type IV isotherms (IUPAC) with clear H1-type adsorption-desorption hysteresis loops. Herein, it is noteworthy that the narrow H1-type hysteresis loop is maintained after the polymer impregnation. Such an H1-type hysteresis loop exhibiting a sharp change in adsorbed volume around $P/P_0 = 0.6-0.7$ is characteristic of uniform mesopores with open cylindrical geometry [31]. Consequently, the portion of Nafion resin that has been able to penetrate into the porous framework seems to be homogeneously deposited along the cylindrical mesoporous channels. Otherwise, if Nafion resin had been placed within the mesoporous structure in form polymeric aggregates providing different wall thicknesses, the polymer-silica composite material would have exhibited a broader hysteresis loop in the N_2 isotherm [32].

Structural parameters deduced from nitrogen isotherms and XRD patterns of the synthesized materials are shown in Table 1. As it can be seen, there is a gradual reduction of the BET surface area and pore volume with the increase of Nafion content. This decrease must be partially related to the deposition of the polymer over the external surface of mesostructured silica particles. However, it is remarkable the significant reduction of the micro-mesopore/total pore volumes ratio of the Nafion(20)/SBA-15 sample with the highest Nafion content. Whereas similar values or small differences of micro-mesopore/total pore volumes ratios are found for Nafion(15)/SBA-15, Nafion(10)/SBA-15 and pure SBA-15 silica samples, the Nafion(20)/SBA-15 sample displayed a significant reduction down to 62%. This decrease is indicative of a more pronounced blockage of the mesoporous framework by the external coating of the silica particles with the polymer.

Table 1. Physicochemical properties for Nafion-modified mesostructured materials.

Sample	S_{BET} (m^2/g)	V_p^a (cm^3/g)	$V_{mic+mes}^b$ (cm^3/g)	$V_{mic+mes}/V_p$ (%)	D_p^a (nm)	d_{100}^c (nm)	Wall Thickness ^d (nm)
SBA-15	675	1.06	0.8	75.5	8.9	9.5	2.1
Nafion(10)/SBA-15	601	0.91	0.69	75.8	8.7	9.5	2.3
Nafion(15)/SBA-15	490	0.80	0.57	71.2	8.4	9.6	2.7
Nafion(20)/SBA-15	432	0.71	0.44	62.0	8.3	9.6	2.8

^a Total pore volume and pore size calculated by BJH method. ^b Microporous and mesoporous volume estimated by t-plot method. ^c $d(100)$ spacing, measured from small-angle X-ray diffraction. ^d Pore wall thickness calculated as the difference between the lattice parameter (a_0) and the mean pore diameter (D_p), being $a_0=2d(100)/\sqrt{3}$.

Barrett-Joyner-Halenda (BJH) analysis [33] of nitrogen adsorption-desorption isotherms reveals that the mesopore diameter decreased from ca. 8.9 to 8.3 nm, while the wall thickness increased systematically from 2.1 to 2.8 nm with the incorporation of higher Nafion loadings, which suggests at least a partial deposition of Nafion resin on the pore walls. The mean pore size still remains beyond 8 nm for all the Nafion-modified SBA-15 materials, which keeps the interest of these acid catalysts for potential applications in the treatment of bulky molecules. The pore size distribution of Nafion-modified SBA-15, depicted in Figure 2, shows that impregnations with intermediate and high loadings, Nafion(15)/SBA-15 and Nafion(20)/SBA-15, significantly affect the narrow pore size distribution of the purely siliceous SBA-15 support, leading to broader distributions centered at smaller pore sizes. Thus, the characterization data of micro-mesoporosity along with the pore size distribution seem to suggest that the increase of Nafion loading from 15 to 20 wt% does not promote a wider resin layer over the mesoporous channels, but the external deposition of the polymer over the mesostructured silica particles that would block the entrance of pores.

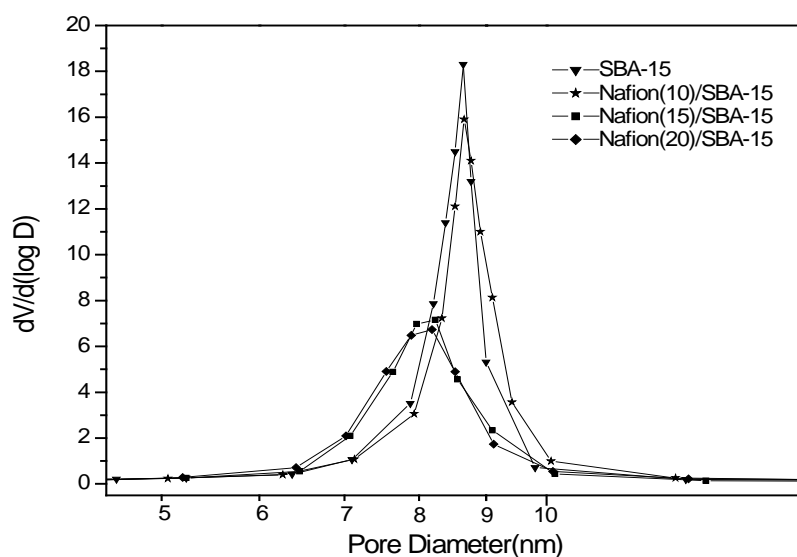


Figure 2. Pore size distributions of the Nafion-modified mesostructured materials.

Table 2 shows several parameters related to the acidic properties of hybrid organic-inorganic Nafion-SBA-15 materials and preliminary catalytic results for the acylation of anisole. Thermogravimetric analyses have been used for the calculation of the Nafion loading. The weight loss between 300 and 550°C was assigned to the thermal decomposition of the organic resin [22]. The final Nafion contents corresponding to

impregnated samples were slightly lower than the pre-fixed nominal values, as it can be deduced from the incorporation yields. On the other hand, the acid capacities of Nafion(10)/SBA-15 and Nafion(15)/SBA-15 samples, in terms of mmol of H⁺/g of catalyst, are surprisingly higher than the sulfur content, in terms of mmol of S/g of catalyst. However, these differences could be related to the intrinsic uncertainty of the elemental analysis when dealing with samples of low sulfur content. These results evidence the incorporation of the organic perfluorosulfonated resin over highly accessible locations, not being entrapped within the micropore system of the SBA-15 [34], where they would not be so accessible. However, in the case of Nafion(20)/SBA-15, the acid capacity in terms of the titration tests remains somewhat below the sulfur content, which indicates a partial lack of accessibility to the acid sites. A feasible explanation of these results could be associated with the partial coating of the mesostructured silica particles by the Nafion resin. This would lead to hindrances in the access to the internal perfluorosulfonated acid sites within the mesoporous channels, and hence non-active for acid-catalyzed application. This hypothesis is supported by the decrease of the pore volume for the Nafion(20)/SBA-15 sample as compared with Nafion(15)/SBA-15 sample, while similar values of mean pore diameter and wall thickness are observed for both samples (Table 1 and Figure 2). Therefore, the incorporation of high Nafion contents (above 15 wt. %) seems to be less appropriate, leading to significant reductions of the active Nafion loading by the deposition over the external surface of the silica particles, thus limiting the effective role of the mesostructured silica support.

Table 2. Organic incorporation and acidic-related properties of Nafion modified mesostructured materials.

Sample	Nafion incorporation		Acidic properties			Catalytic activity ^f	
	wt% ^a	Yield ^b	(mmol S/g _{cat}) ^c	(mmol H ⁺ /g _{cat}) ^d	Access. ^e	X _{anisole} ^g	Specific Activity ^h
Nafion(10)/SBA-15	9.5	95	0.078±0.013	0.098	100	7.7	751
Nafion(15)/SBA-15	13.1	87	0.125±0.012	0.136±0.02	100	13.7	834
Nafion(20)/SBA-15	17.7	88	0.165±0.016	0.140	85	12.2	563

^a Weight percent of Nafion determined via weight loss by TGA between 300 and 550°C. ^b Yield of incorporation (%) of Nafion referred to theoretical synthesis values. ^c Sulfur content calculated from elemental analysis. ^d Obtained by cationic-exchange in saturated NaCl in ethanol, and titration with NaOH 0.01M. ^e Accessibility to acid sites from sulfur content and titration data (after cationic-exchange). ^f Reaction conditions: 125°C, anisole/catalyst mass ratio 80, equimolar anisole/ac. anhydride ratio, reaction time 5h. ^g Percent conversion of anisole determined by GC. ^h Specific catalytic activity as determined by mmols of reacted anisole within 5 hours of reaction referred to catalyst's sulfur content (mmol of reacted anisole/mmol S)

According to the catalytic performance of Nafion/SBA-15 samples for the acylation of anisole with acetic anhydride in terms of anisole conversion and specific activity, Nafion(15)/SBA-15 sample has been the most effective catalyst. This catalyst has displayed not only the highest conversion of anisole after 5 hours of reaction, but also the best results in terms of the specific activity, with 834 mmol of anisole converted per sulfur site. The highest Nafion content, Nafion(20)/SBA-15, did not lead to the enhancement of the catalytic performance, evidencing even a lower anisole conversion and a remarkable decrease of the specific activity. The activity in terms of anisole conversion is certainly related to the acid capacity which is somewhat comparable to that shown by Nafion(15)/SBA-15. The results of the specific activity confirm a lower availability of the perfluorosulfonic acid sites for the sample with the highest resin content. Concerning the reaction products, a high selectivity towards *p*-methoxyacetophenone (*p*-MAP) was observed for all the materials (over 92.5%), although the presence of minority products such as *o*-MAP or other poly-acetylated by-products were also detected.

Keeping in mind all these characterization data and the preliminary catalytic tests, Nafion(15)/SBA-15 has been selected as the material with the most interesting physicochemical properties for application in the acylation of anisole. Several TEM images of this sample show typical rod-shaped particles of mesoporous materials with hexagonal structure (Figure 3a and 3b). Microphotographs in Figure 3c and 3d allow to

confirm the presence of well-ordered hexagonal channels with a 2D mesostructure of the silica-supported Nafion material with an estimated pore diameter about 8-9 nm. This is in agreement with the pore size obtained by nitrogen adsorption-desorption isotherms. Moreover, it must be noted that polymeric aggregates could not be observed around silica particles, supporting the hypothesis of a homogeneous distribution of the perfluorosulfonic acid resin throughout the external surface area and/or along the mesoporous channels. Local microanalysis by EDX over random ordered regions demonstrated a well-dispersed polymeric resin with F/Si ratios ranging from 0.15 to 0.19.

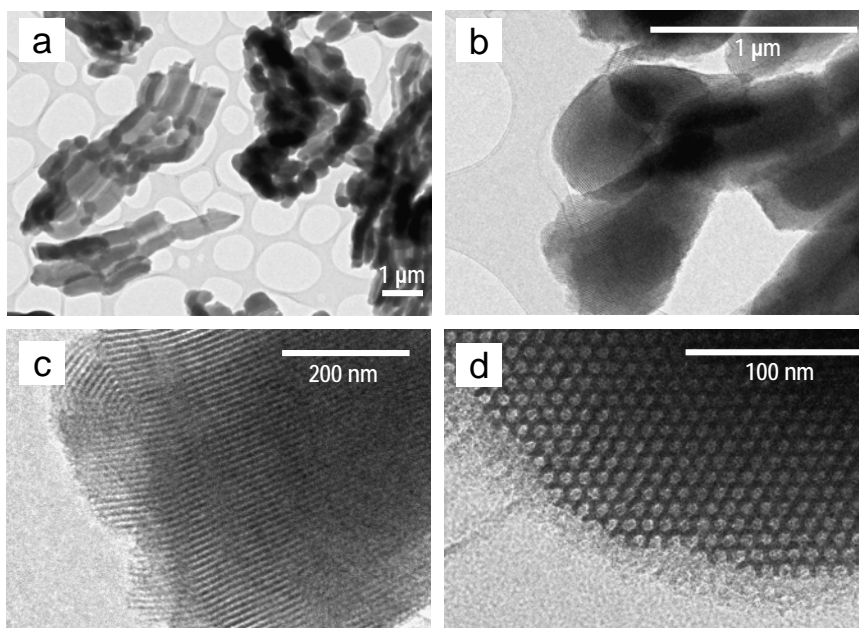


Figure 3. TEM images of Nafion(15)/SBA-15 particles (a and b); and microphotographs viewed (c) in the [100] direction - parallel to the channel direction and (d) in the [110] direction - transversal section of channels.

3.2 Study of the acylation of anisole over Nafion-modified SBA-15

Preliminary experiments of Nafion-modified SBA-15 acid solid catalysts with different resin contents for the acylation of anisole have demonstrated a significant influence of their physicochemical properties on the catalytic performance, depending on the amount of Nafion that is loaded over the silica support. In this second part of the work, the influence of two variables of reaction, the anisole/anhydride acetic ratio and the temperature in solventless reaction conditions, has been studied using the silica SBA-15 support with the optimum resin loading, Nafion(15)/SBA-15. A factorial design of experiments based on a 3^2 model [35] was selected considering three levels for

each variable: X, anisole to acetic anhydride molar ratio (An/AA; 1:1, 1:2, and 1:3) and Y, the reaction temperature (100, 125 and 150°C). The choice of non-solvent anisole acylation has been assumed not only to avoid the known environmental disadvantages of using a solvent, but also to overcome the lower conversions and faster deactivation of the catalyst when using polar solvents such as nitrobenzene or nitromethane [36]. The range of reaction temperature was selected on the basis of previous studies of anisole acylation using MCM-41 and SBA-15 silicas functionalized with perfluorosulfonic acid groups [26], H-form of Beta, Y and ZSM-5 zeolites [37], and arenesulfonic acid-modified mesostructured SBA-15 [38]. The range of An/AA ratio was set between acetic anhydride-rich mixtures and equimolar ratios, considering anisole as limiting substrate [39], although other studies have also proposed anisole-rich mixtures rather than equimolar ratios in order to slow down the catalyst deactivation rate [36].

Table 3 summarizes the results coming from the factorial design of experiments, including the codified and real values of reaction conditions. Low and high levels of each variable are denoted as -1 and +1, respectively, whereas the central value of the variable is codified as 0. The experiment corresponding to the conditions of the central point of the design (125°C and 1:2 anisole/acetic anhydride molar ratio) was repeated three times. The conversion of anisole (%) at different reaction times is selected as the response factor for the evaluation of the catalytic performance. Assuming a second order polynomial equation and using a Levenberg-Marquard algorithm for non-linear regression, equations [1] and [2] were deduced for 1h and 5h of reaction, being X and Y the anisole to acetic anhydride molar ratio and reaction temperature, respectively. Experimental and predicted results of the anisole conversion from the model are shown in Table 3 and compared in Figure 4.

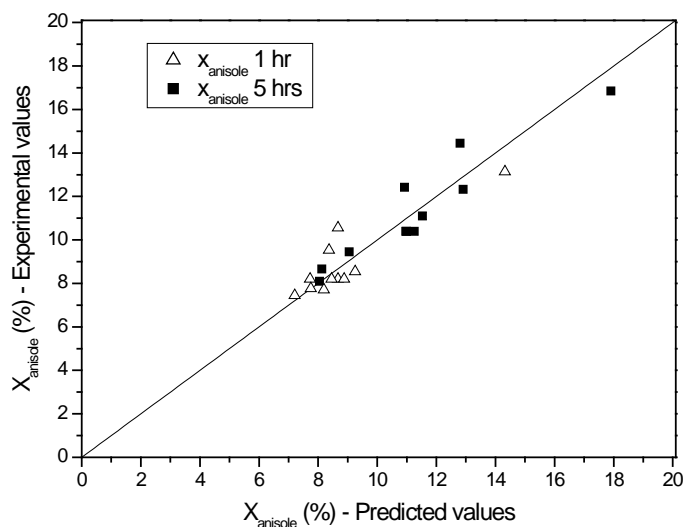
$$Z_1 (X_{\text{anisole}}, \%) = 8.20 - 1.04X + 1.43Y - 1.26XY + 0.28X^2 + 0.92Y^2 \quad [1]$$

$$Z_2 (X_{\text{anisole}}, \%) = 10.39 + 1.88X + 2.50Y + 0.38XY + 0.15X^2 + 1.55Y^2 \quad [2]$$

Table 3. Numerical data and results of the factorial design for the acylation of anisole.

Run ^a	An:AA molar ratio (X)	T (°C) (Y)	Z = X _{anisole} (%)			
			Z ₁ (1h)		Z ₂ (5h)	
			Exp ^b	Calc ^c	Exp ^a	Calc ^b
1	1:3 (-1)	100 (-1)	7.73	8.20	8.05	8.09
2	1:3 (-1)	125 (0)	7.21	7.45	8.12	8.66
3	1:3 (-1)	150 (+1)	9.25	8.54	12.90	12.33
4	1:2 (0)	100 (-1)	8.20	7.70	9.05	9.45
5	1:2 (0)	125 (0)	8.67	8.20	10.97	10.39
6	1:2 (0)	125 (0)	8.88	8.20	11.25	10.39
7	1:2 (0)	125 (0)	8.46	8.20	10.99	10.39
8	1:2 (0)	150 (+1)	8.67	10.56	12.81	14.44
9	1:1 (+1)	100 (-1)	7.75	7.77	11.53	11.09
10	1:1 (+1)	125 (0)	8.37	9.53	10.93	12.42
11	1:1 (+1)	150 (+1)	14.32	13.14	17.91	16.85

^a Experiments with anisole/catalyst weight ratio = 80; catalyst: Nafion(15)/SBA-15. ^b Experimental results. ^c Calculated values from equations [1] and [2].

**Figure 4.** Accuracy of the predicted data versus the experimental results for the anisole conversion at different reaction times.

Concerning the equation coefficients, the presence of quadratic terms allowed a better fitting of the mathematical equations to the experimental results, giving also a certain curvature to the response surfaces illustrated in Figure 5. Coefficients related to the influence of reaction temperature (Y and Y²) have more influence than those corresponding to the anisole/acetic anhydride molar ratio (X and X²). The results of the experiments performed in the reaction conditions of the central point (125 °C,

An/AA=1/2) provide the standard deviations of the anisole conversion at 1 and 5 hours of reaction, which indicate that variations of the anisole conversion lower than 2% in our experiments must be carefully discussed because these catalytic performances would be within the experimental error. The 3D graphical representations of equations [1] and [2] are illustrated in Figure 5. The influence of both studied variables on the conversion of anisole is more evident after 5 hours. Nevertheless, the reaction temperature shows a predominating effect on the catalytic performance as compared with the An/AA molar ratio. Thus, a remarkable enhancement of the anisole conversion can be observed as the reaction temperature increases, regardless of the rich-acetic anhydride reaction mixture. In contrast, the increase of the anisole/acetic anhydride molar ratio from 1:3 to equimolar 1:1 mixture evidences a lesser contribution on the catalytic performance.

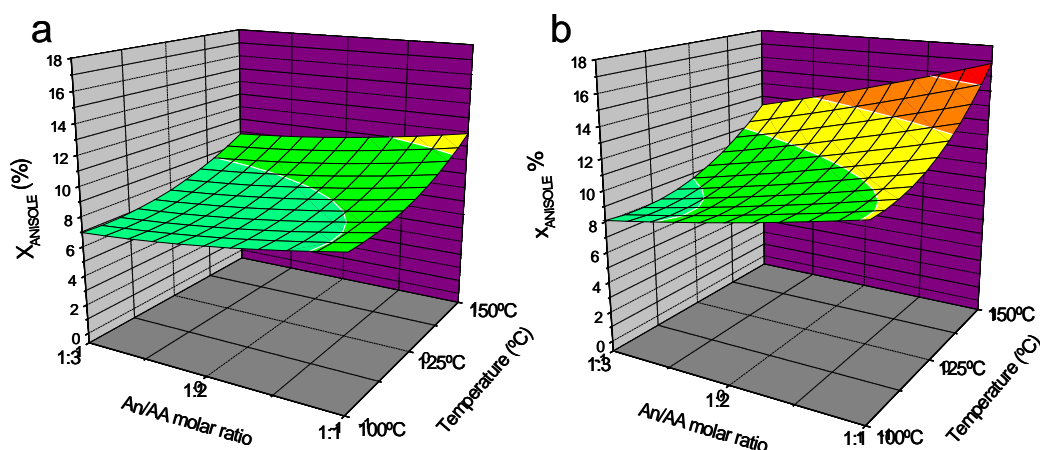


Figure 5. 3D response surface of anisole conversion at 1 hour (a) and 5 hours (b) of reaction. Anisole/catalyst weight ratio = 80; catalyst: Nafion(15)/SBA-15.

The small difference between the independent terms of equations [1] and [2] for 1 hour and 5 hours of reaction can be associated with the fast catalyst deactivation that classically occurs in acid-catalyzed acylation reactions by the interaction of *p*-methoxyacetophenone and/or multiple poly-acetylated products with the catalytic acid sites at short reaction times [40-42]. In this sense, small increases in anisole conversion can be obtained for longer reaction times. This deactivating phenomenon appears to be more pronounced for less favourable reaction conditions – the lowest temperature, 100 °C and acetic anhydride-rich mixture of 1:3 – wherein the anisole conversion,

considering the experimental error above mentioned, practically does not increase between 1 h and 5 h of reaction (from 7.3% to 8.0%). In the best reaction conditions of this set of experiments – the highest temperature, 150°C, and equimolar anisole/Acetic anhydride molar ratio – a higher increase in anisole conversion is obtained, from 14.3% at 1 h to 17.9% at 5h of reaction. From the point of view of the reaction media composition, these results seem to demonstrate the negative role of acetic anhydride-rich mixtures by the formation of poly-acetylated compounds that are actively involved in the catalyst deactivation. Nevertheless, it must be reminded that the catalyst deactivation is not only restricted to poly-acetylated products but also to the strong adsorption of *p*-methoxyacetophenone as main product of the anisole acylation [41]. The selectivity towards the *p*-methoxyacetophenone ranged from 92.5 to 95.5 %. These high values of *para*-selectivity come from the activation of the *para*-position for electrophilic substitution, independently of using very different catalysts in homogeneous or heterogeneous reaction media [41-43]. Within the reaction conditions here studied, a small increase of *para*-selectivity was detected for the lowest temperature (100°C) with ca. 95% as compared to 150°C with ca. 92%. In contrast, the influence of the anisole/acylating agent molar ratio on the *para*-selectivity was found negligible.

3.3 Comparison with other solid perfluorosulfonic acid-based catalysts

The promising catalytic properties of Nafion(15)/SBA-15 material for the anisole acylation have been compared with the activity of other perfluorosulfonic acid-based catalysts found in literature: i) the commercial Nafion[®]-SAC-13 and ii) so-called SFS material as described in the experimental section. The three materials were tested at 150°C and equimolar An:AA molar ratio. Figure 6 shows the catalytic performance of each acid material in terms of anisole conversion along the reaction time, whereas their most relevant textural and catalytic properties are summarized in Table 4.

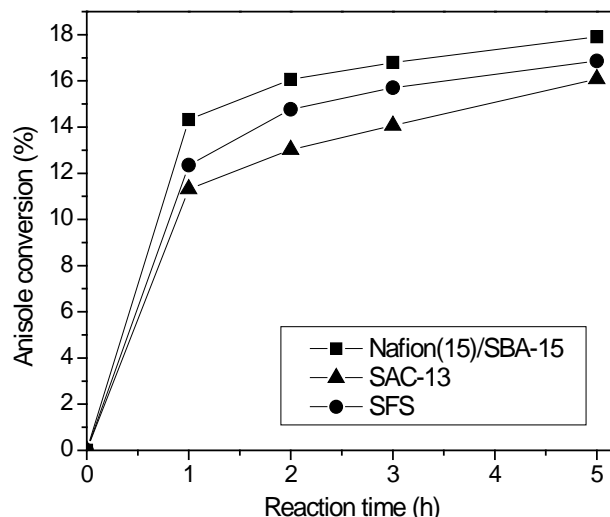


Figure 6. Catalytic performance of perfluorosulfonic acid-based catalysts. Reaction conditions: T, 150°C; Equimolar An/AA ratio; An:Cat mass ratio, 80.

A higher catalytic performance is obtained for the Nafion(15)/SBA-15 compared to either the SAC-13 material with the perfluorosulfonic Nafion resin supported over an amorphous silica via sol-gel techniques, or so-called SFS with perfluorosulfonic acid functionalization over mesoporous SBA-15 silica via reactive-grafting. It must be pointed out that all the three catalysts displayed similar profiles with a significant decay of the anisole conversion due to the catalyst deactivation as discussed in the earlier section.

Table 4. Textural and catalytic properties of perfluorosulfonic acid-based catalysts.

Sample	Textural properties			Catalytic properties		
	S_{BET} (m ² /g)	$V_{\text{pore}}^{\text{a}}$ (cm ³ /g)	$D_{\text{pore}}^{\text{a}}$ (Å)	mmol S/g _{cat} ^b	mmol H ⁺ /g _{cat} ^c	Initial Specific Activity ^d
Nafion(15)/SBA-15	490	0.80	84	0.125	0.136	848
SAC-13 ^e	201	0.43		0.143	0.132	585
SFS	442	0.81	96	0.284	na*	322

^a Total pore volume and pore size calculated by BJH method. ^b Sulfur content calculated from elemental analysis. ^c Obtained by cationic-exchange in saturated NaCl in ethanol, and titration with NaOH 0.01M. ^d Specific catalytic activity calculated as mmols of reacted anisole for 1h of reaction referred to catalyst's sulfur (mmol of reacted anisole/mmol S). ^e SAC-13 commercial catalyst was ground with a mortar in order to achieve similar particle size to that powder Nafion(15)/SBA-15 and SFS samples and avoid diffusional limitations. * Non-available.

However, a more precise analysis of the catalytic activity should be done by evaluation of the acid sites density and the textural properties of each material. It must be taken into account that acid site densities in terms of mmol of S / g of catalyst are representative of all the sulfonic acid sites in the bulk sample, whereas the values in terms of mmol H⁺/g_{cat} help to quantify the amount of accessible sulfonic acid sites.

However, due to non-satisfactory measurements of the acid capacity in terms of mmol H^+ / g_{cat} for the SFS sample by the titration method, the specific activity for the anisole acylation was calculated as mmol of reacted anisole per mmol of S. On this basis, the specific activity was given at the shortest reaction time available, 1 hour, in order to minimize deactivation effects (see Table 4). Nafion(15)/SBA-15 is shown much more effective than the other two catalysts, achieving values higher than 800 mmol of converted anisole per mmol of S, in contrast to the values for SAC-13 and SFS catalysts. Nevertheless, although variations between the acid site densities in terms of mmol H^+ / g_{cat} and mmol S/ g_{cat} can be considered to fall within the uncertainty of those analytical techniques when such low sulfur contents are measured, it must be noted that values of the specific activity as mmol of reacted anisole per mmol of H^+ would make the specific activity of SAC-13 slightly closer than that of Nafion(15)/SBA-15 (779 and 634 mmols of reacted anisole per mmol of H^+ , respectively). In any case, since both materials have the same type of acid moieties based on perfluorosulfonic Nafion resin, a better availability of acid sites seems to be achieved in the mesostructured silica SBA-15 support, probably as result of a better dispersion of the polymeric resin over its extended surface area (490 m^2/g). In the case of the SFS material, with similar textural properties to the Nafion(15)/SBA-15 sample, it is noteworthy that a higher sulfur content has not led to the improvement of the catalytic performance. This fact suggests a lower activity of the acid sites or the presence of entrapped acid sites that are less accessible for the effective acylation of anisole. This might be related to the sultone ring-opening reaction that occurs for the anchoring of the perfluorosulfonic acid precursor [26].

Additional Friedel-Crafts acylation based on the Fries rearrangement of phenyl acetate to produce acylated phenols was tested in order to assess the acid catalytic activity of perfluorosulfonic Nafion acid resin supported over hexagonally mesoporous SBA-15 silica support versus the other reference perfluorosulfonic acid-based catalysts (SAC-13 and SFS). The combined yields to the most desired products (*o*- and *p*-hydroxyacetophenones; *o*-HAP and *p*-HAP) and non-desired *p*-acetoxyacetophenone by-product (*p*-AXAP) [44], as well as individual selectivities –excluding phenol due to its co-solvent condition- for each acetophenone are shown in Table 5. The catalytic results confirm that the Nafion-mesostructured SBA-15 silica material also constitutes a competitive alternative for a more complex acid-catalyzed reaction. Nafion(15)/SBA-15

provides the highest yield to acetophenones, accompanied by a reduced selectivity toward the non-desired *p*-AXAP. Thus, the activity and selectivity of Nafion(15)/SBA-15 towards desired *p*- and *o*-HAP seem to be enhanced by the physicochemical properties of the Nafion resin supported over the mesostructured SBA-15 silica instead of a non-ordered silica. Moreover, these results are really valuable as compared to the data found in literature for a perfluorosulfonic acid catalyst prepared by impregnation of 10 wt% Nafion over non-ordered silica, where a low activity was reported in this particular reaction by the so-called Nafion-H/SiO₂ impregnated catalyst with a negligible production of *p*-HAP and *o*-HAP in contrast to the SAC nacomposite [45]. In that case, the higher activity of SAC nacomposite was also related to its increased accessibility of surface-active sites to reactants, ensured by the large surface area of the silica matrix.

Table 5. Comparison of the catalytic performance of perfluorosulfonic acid-based catalysts in the Fries rearrangement of phenyl acetate. Reaction conditions: 150°C; phenyl acetate (PAC) 10g; Phenol 5g; Catalyst 0.25g. Reaction time: 5 hours.

Catalyst	AP Yield (%) ^a	Selectivity (%) ^b		
		<i>p</i> -Hydroxyacetophenone (<i>p</i> -HAP)	<i>o</i> -Hydroxyacetophenone (<i>o</i> -HAP)	<i>p</i> -Acetoxyacetophenone (<i>p</i> -AXAP)
Nafion(15)/SBA-15	4.69	53.7	25.8	20.5
SAC-13	4.10	44.1	18.0	37.9
SFS	1.01	1.0	99.0	0.0

^a Combined yield to acetophenones (*p*-HAP, *o*-HAP and *p*-AXAP). ^b Selectivities calculated as (mmol of the corresponding product / mmol of total products excluding phenol) x 100.

3.4 Stability of Nafion-impregnated mesoporous SBA-15 materials in the acylation of anisole

As mentioned earlier, the main deactivation of solid acid catalysts is due to the formation of poly-acylated products that are strongly adsorbed over the active sites. However, the leaching of perfluorinated Nafion resin into the liquid phase could take place during the acylation reaction, misleading the interpretation of the results. In order to check the stability of immobilized Nafion resin and the contribution of the leached acidic moieties, an additional homogeneous test was carried out as follows: i) a normal catalytic assay was started at 150°C and equimolar An:AA molar ratio with the catalyst Nafion(15)/SBA-15; ii) after 1 hour of reaction, the catalyst was hot-separated by filtration; and iii) the resultant solution was introduced again into the reactor vessel

keeping the reaction continuing up to 5 hours in absence of the solid catalyst. The anisole conversion for the catalytic system using Nafion(15)/SBA-15 and the so-called homogeneous test (after removal of catalyst at 1 h) are shown in Figure 7. As it can be seen, once the solid Nafion(15)/SBA-15 was removed from the reaction media, the conversion of anisole kept constant for the homogeneous test in contrast to the heterogeneous catalytic system. These results suggest that there is no leaching of active perfluorosulfonic acid moieties to the liquid medium, so anisole conversion by homogeneously acid-catalyzed reactions can be discarded.

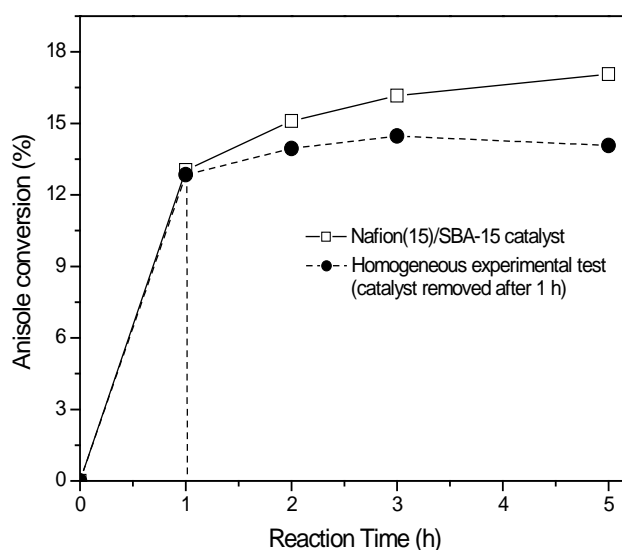


Figure 7. Stability of Nafion(15)/SBA-15 material for the acylation of anisole. Reaction conditions: T, 150°C; Equimolar An/AA ratio; An/Cat mass ratio, 80.

Thermogravimetric analyses (TGA) on fresh and spent catalysts were also performed in order to quantify any possible loss of Nafion resin in the recovered catalyst after reaction. TGA profiles of both samples are shown in Figure 8. For the fresh catalyst, the main weight loss takes place around 425°C and accounts exclusively for the thermal decomposition of the Nafion resin [22]. It is noteworthy a high temperature of combustion for the Nafion resin when it is supported over the SBA-15 silica support via impregnation. Thus, in the particular case of Nafion(15)/SBA-15, the weight loss ranging from 300°C to 550°C is ca. 0.15 grams per gram of SiO₂. The residual silica weight of the sample at 700°C was used as reference for determining the total organic loading. For the spent catalyst, two significant weight losses are clearly evident at 150°C and 425°C. The former, predominant, is associated with reactants and acetylated products that are adsorbed over the catalyst surface soaking the pore system.

The latter appears at the temperature range where Nafion decomposes (300-550°C), reaching up to 0.22 grams of organic matter per gram of silica. Hence, the increase of weight loss in this range confirms the absence of leaching of Nafion and the presence of strongly chemisorbed by-products over the acid sites of catalyst. These chemisorbed by-products, probably poly-acetylated compounds, are supposed to be mainly responsible of the catalyst deactivation.

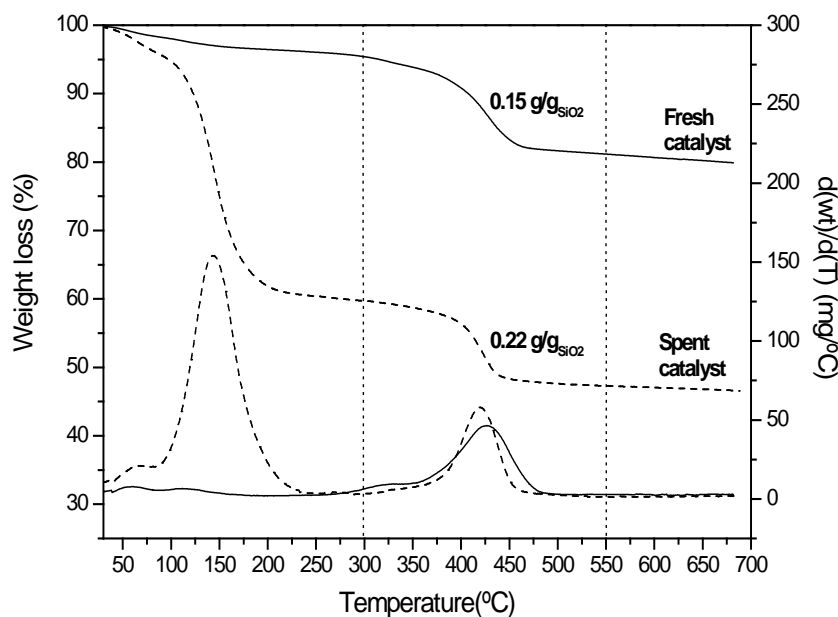


Figure 8. Thermogravimetric analyses of fresh and spent Nafion(15)/SBA-15 catalysts.

All these results also prove an adequate interaction between the polymeric perfluorosulfonic resin and the mesoporous SBA-15 silica support that prevent the re-dissolution of Nafion into the reaction medium. Moreover, the loss of activity by deposition of poly-acetylated products on the active acid sites of Nafion/SBA-15 materials for the acylation of anisole is suggested.

3.5 Regeneration of the catalyst

The regeneration of spent hybrid organic-inorganic catalysts after anisole acylation by mild calcination at 200 °C or extraction with ethanolic solutions have resulted non-effective, recovering hardly 5% of initial activity [36, 38]. Recently, a treatment based on the extraction with a boiling HNO₃ solution has been claimed as efficient method in the regeneration of SAC-13-type catalysts [36], although not further characterization on

the regenerated catalysts was presented. Herein, spent Nafion(15)/SBA-15 and SAC-13 catalysts have been regenerated by extraction with 20 wt% HNO₃ solution under reflux. Prior to this, the catalysts were washed with acetone in order to remove all the weakly adsorbed reactants and products that remain within the pore structure after reaction. Following the acid extraction under reflux, the resultant suspension was cooled down and the solid catalysts were recovered by filtration and washed successively with water until neutral pH. The catalytic performance of fresh and regenerated catalysts is illustrated in Figure 9. As it can be seen in this Figure, a noteworthy recovery of the catalytic activity for both Nafion-containing materials was attained, achieving ca. 93% and 80 % of the initial catalytic activity of Nafion(15)/SBA-15 and SAC-13 catalysts, respectively.

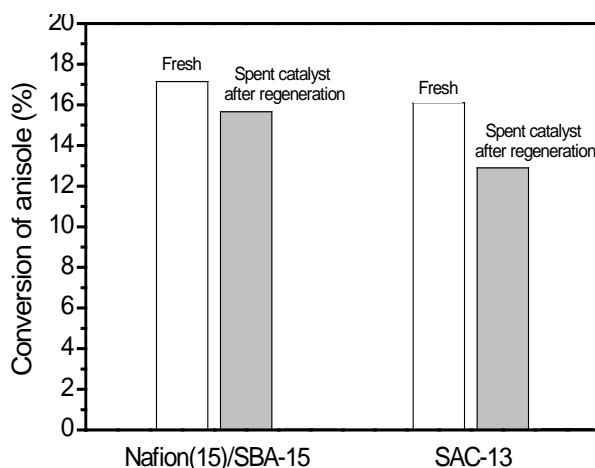


Figure 9. Catalytic activity of fresh and regenerated Nafion-containing catalysts. Reaction conditions: T, 150°C; Equimolar An/AA ratio; An/Cat mass ratio, 80.

Thermogravimetric analysis of regenerated Nafion(15)/SBA-15 catalyst has revealed the extraction of labile reactants present in the spent catalyst (negligible weight loss at ca. 150 °C, Figure 10). However, in the range of 300-550°C, the weight loss of the catalyst after regeneration is higher, ca. 0.28 g/g_{SiO₂}, than that of the spent catalyst after reaction, ca. 0.22 g/g_{SiO₂}. Thus, these results indicate that deactivating by-products strongly chemisorbed in the proximity of perfluorosulfonic acid sites are quite difficult to extract. However, measurements of the acid capacity revealed a total recovery of the acid capacity for the regenerated Nafion(15)/SBA-15 catalyst with 0,142 mmol of H⁺ per g of catalyst as compared with that shown by the fresh catalyst, 0,136 mmol of H⁺ per g of catalyst. Note that this slight increase is not relevant and would be within the

uncertainty of the titration method. Moreover, elemental analysis of the spent catalyst after regeneration evidenced similar sulfur contents than the fresh catalyst, but also revealed the presence of nitrogen (0.3 wt%). Thus, there is no doubt that perfluorosulfonic acid sites are not extracted during the regeneration process and traces of nitric acid are still present inside the mesoporous matrix. As mineral nitric acid could be active in acid-catalyzed reactions, a homogeneous test was performed using nitric acid with an Anisole/nitric acid mass ratio of 80 at 150°C and equimolar An/AA ratio. The anisole conversion remained lower than 0.5% after 5 hours of reaction, demonstrating the negligible activity of nitric acid in the selected reaction conditions. This result discarded the participation of homogenous nitric acid species in the catalytic acylation of anisole.

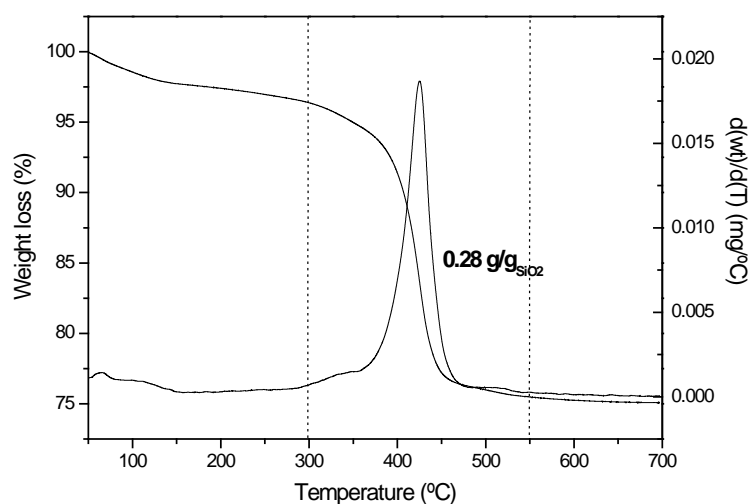


Figure 10. Thermogravimetric analysis of regenerated Nafion(15)/SBA-15.

A similar treatment with nitric acid under reflux was performed with a fresh catalyst sample. In this case, the organic content did not essentially change in the range of 300-550°C – from 0.15 g/g_{SiO₂} for the fresh catalyst to 0.14 g/g_{SiO₂} for the treated sample – and no nitrogen was detected by elemental analysis. This suggests that Nafion resin itself does not promote any interaction with nitric acid leading to nitrogen-free Nafion-containing-catalyst. Therefore, the mentioned increase of weight loss of the spent catalyst from 0.22 g/g_{SiO₂} to 0.28 g/g_{SiO₂} after regeneration seems to be associated with the presence of the deactivating by-products strongly chemisorbed in the proximity of perfluorosulfonic acid sites. Thus, since the extraction of the deactivating by-products was not achieved by the nitric acid treatment, and homogeneous activity of trapped

nitric acid on the solid catalyst was ruled out, a plausible explanation of the regained catalytic activity of Nafion-based catalysts could be related to the displacement of strongly chemisorbed by-products from the active perfluorosulfonic acid sites during the nitric acid regeneration. Nevertheless, further studies need to be performed to elucidate the mechanism involved in the reactivation of perfluorosulfonic acid by the treatment with nitric acid.

4. Conclusions

Perfluorosulfonic acid Nafion resin has been successfully supported over mesostructured SBA-15 materials by means of impregnation with different resin contents. An optimal Nafion loading has been achieved by Nafion(15)/SBA-15 material with ca. 13 wt% of Nafion. This sample has been the most effective in the acylation of anisole on the basis of its physicochemical properties, remarkable surface area (490 m²/g) and narrow pore size distribution centred at the mesoscale range (8 nm). The increase of Nafion loadings above 15 wt. % has not promoted an enhancement of the catalytic performance, possibly due to the loss of the SBA-15 silica mesoporosity by the dominant deposition of the Nafion resin over the external surface of the silica particles, thus limiting the effective role of the mesostructured silica support.

A factorial design of experiments for the evaluation of the reaction temperature and the anisole to acetic anhydride ratio in solventless reaction conditions has demonstrated a dominant role of the temperature rather than the ratio of reactants. The sample denoted as Nafion(15)/SBA-15 has shown the best catalytic performance using an equimolar anisole to acetic anhydride molar ratio at 150°C. The catalytic activity of this material has been superior to those of other perfluorosulfonic acid-based catalysts, such as the commercial Nafion[®]-SAC-13 or SFS material prepared by reactive-grafting of perfluoroalkylsulfonic acid precursors over SBA-15 mesoporous silica. The characterization data of Nafion(15)/SBA-15 catalyst before and after reaction have evidenced a high stability of the impregnated material, although a remarkable deactivation was observed by strongly chemisorbed poly-acetylated by-products. Additionally, an outstanding regeneration of the catalyst was achieved by the treatment with nitric acid, regaining 93% of the initial catalytic activity of the fresh catalyst.

References

- [1] A. Corma and H. García, *Chem. Rev.* 103 (2003) 4307.
- [2] R.A. Sheldon and H. Van Bekkum, "Chemicals through Heterogeneous Catalysis", Wiley-VCH, Weinheim, 2001.
- [3] A. Corma and H. García, *Catal. Today* 38 (1997) 257.
- [4] W. F. Hölderich, M. Hesse, F. Näumann, *Angew. Chem., Int. Ed. Engl.* 27 (1988) 226.
- [5] A. Corma, M. T. Navarro, J. Pérez-Pariente, *J. Catal.* 148 (1994) 569.
- [6] (a) J. A. Melero, R. van Grieken, G. Morales, *Chem. Rev.* 106 (2006) 3790; (b) A. Molnar and B. Rac, *Curr. Org. Chem.*, 10 (2006) 1697.
- [7] W. M. Van Rhijn, D. E. De Vos, B. F. Sels, W. D. Bossaert, P. A. Jacobs, *Chem. Commun.* (1998) 317.
- [8] M. H. Lim, C. F. Blanford, A. Stein, *Chem. Mater.* 10 (1998) 467.
- [9] K. Wilson, A. F. Lee, D. J. Macquarrie, J. H. Clark, *Appl. Catal., A* 228 (2002) 127.
- [10] D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* 12 (2000) 2448.
- [11] M.J. Meziani, J. Zajac, D.J. Jones, S. Partyka, J. Roziere, A. Auroux, *Langmuir* 16 (2000) 2262.
- [12] D. Brunel, A.C. Blanc, A. Galarneau, F. Fajula, *Catal. Today* 73 (2002) 139.
- [13] J. A. Melero, G. D. Stucky, R. van Grieken, G. Morales, *J. Mater. Chem.* 12 (2002) 1664.
- [14] I. K. Mbaraka, B. H. Shanks, *J. Am. Oil. Chem. Soc.* 83 (2006) 79.
- [15] M. A. Harmer, Q. Sun, *Appl. Catal. A* 221 (2001) 45.
- [16] G. A. Olah, P. S. Iyer, G. K. Suryaprakash, *Synthesis* (1986) 513.
- [17] M. A. Harmer, W. E. Farneth, Q. Sun, *Adv. Mater.* 10 (1998) 1255.

- [18] M. A. Harmer, Q. Sun, A. J. Vega, W. E. Farneth, A. Heidekum, W. F. Hölderich, *Green Chem.* 2 (2000) 7.
- [19] P.F. Siril, A.D. Davison, J.K. Randhawa, D.R. Brown, *J. Mol. Catal. A: Chemical* 267 (2007) 72.
- [20] G. A. Olah, R. Malhotra, S. C. Narang, J. A. Olah, *Synthesis* (1978) 672.
- [21] F. J. Waller, R. W. van Scoyoc, *CHEMTEC* 17 (1987) 438.
- [22] A. Molnar, *Curr. Org. Chem.*, 12 (2008) 159.
- [23] A. Heidekum, M. A. Harmer, W. F. Hölderich, *J. Catal.* 176 (1998) 260.
- [24] S. Wang and J. A. Guin, *Energy & Fuels* 15 (2001) 666.
- [25] M. Harmer., Q. Sun, M. J. Michalczyk, Z. Yang, *Chem. Commun* (1997) 1803.
- [26] (a) M. Alvaro, A. Corma, D. Das, V. Fornés, H. García, *Chem. Commun.* (2004) 956. (b) M. Alvaro, A. Corma, D. Das, V. Fornés, H. García, *J. Catal.* 231 (2005) 48.
- [27] D. J. Macquarrie, S. J. Tavener, M. A. Harmer, *Chem. Commun.* (2005) 2363.
- [28] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrikson, B. F. Chmelka, G. D. Stucky, *Science* 279 (1998) 548.
- [29]. W. Hammond, E. Prouzet, S. D. Mahanti; T. J. Pinnavaia, *Microporous Mesoporous Mater.* 27 (1999) 19.
- [30] B. Smarsly, C. G. Goltner, M. Antonietti, W. Ruland, E. Hoinkis, *J. Phys. Chem. B.* 105 (2001) 831.
- [31] M. Kruk, M. Jaroniec; S. H. Joo, R. Ryoo, *J. Phys. Chem. B.* 107 (2003) 2205.
- [32] M. Choi, F. Kleitz, D. Liu, H. Y. Lee, W. S. Ahn, and R. Ryoo *J. Am. Chem. Soc.* 127 (2005) 1924.
- [33] E. P. Barrett, L. G. Joyner, P. P. Halenda, *J. Am. Chem. Soc.* 73 (1951) 373.
- [34] R. van Grieken, G. Calleja, G. D. Stucky, J. A. Melero, R. A. García, J. Iglesias, *Langmuir* 19 (2003) 3966.

- [35] G. E. P. Box, W. G. Hunter, J. S. Hunter, "Statistics for Experiments, an Introduction to Design, Data Analysis and Model Building", Wiley, New York, 1978.
- [36] V. R. Sarsani, C. J. Lyon, K. W. Hutchenson, M. A. Harmer, B. Subramaniam, J. Catal. 245 (2007) 184.
- [37] U. Freese, F. Heinrich, F. Roessner, Catal. Today 49 (1999) 237.
- [38] J. A. Melero, R. van Grieken, G. Morales, V. Nuño, Catal. Commun. 5 (2004) 131.
- [39] G. D. Yadav and M. S. M. M. Rahuman, Org. Process Res. Development 6 (2002) 706.
- [40] D. Rohan, C. Canaff, E. Fromentin, M. Guisnet, J. Catal. 177 (1998) 296.
- [41] E. G. Derouane, C. J. Dillon, D. Bethell, S. B. erouane-Abd Hamid, J. Catal. 187 (1999) 209.
- [42] L. A. M. Cardoso, W. Alves, A. R. E. Gonzaga, L. M. G. Aguiar, H. M. C. Andrade, J. Mol. Catal. A 209 (2004) 189.
- [43] Yubin Yuan, Jin Nie, Zhengbo Zhang, Shuojin Wang, Appl. Catal. A: Gen. 295 (2005) 170.
- [44] R. van Grieken, J. A. Melero, G. Morales, Appl. Catal. A 289 (2005) 143.
- [45] B. Török, I. Kiricsi, A. Molnar, G. O. Olah, J. Catal. 193 (2000) 132.