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Journal of Catalysis 231 (2005) 48–55

JOURNAL OF CATALYSIS

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"*Nafion*"-functionalized mesoporous MCM-41 silica shows high activity and selectivity for carboxylic acid esterification and Friedel–Crafts acylation reactions

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Received 10 November 2004; revised 23 December 2004; accepted 10 January 2005

Abstract

Hybrid organic–inorganic MCM-41 silicas functionalized with perfluoroalkylsulfonic acid groups analogous to that of Nafion were prepared in a simple single step by a condensation reaction between surface silanol groups of the mesoporous silicas and 1,2,2-trifluoro-2-hydroxy-1-trifluoromethyl-ethane sulfonic acid Beta-sultone. The catalysts showed very high activity for the esterification of long-chain fatty acids with ethanol and high-molecular-weight alcohols with essentially complete selectivity at high conversion (> 95%). Acylation of anisole was also possible, with high selectivity for 4-methoxyacetophenone. The catalysts showed more activity conversion than commercial Nafion–silica composite catalysts.

Keywords: Perfluorosulfonic acid; Nafion; MCM-41; Esterification; Fatty acids; Acylation; Anisole

1. Introduction

Acid-catalyzed carboxylic acid esterification and Friedel–Crafts acylation reactions are important synthetic reactions for the preparation of key organic value-added intermediates [1]. Preparation of alkyl esters and acylated aromatic ketones is of particular importance in the manufacture of intermediates for the fragrance and pharmaceuticals industries [2–4]. In normal practice, strong mineral acids, such as H_2SO_4, HF, or supported Lewis-acid catalysts like anhydrous $AlCl_3/SiO_2$ and BF_3/SiO_2, are used for such reactions. However, the use of corrosive mineral acids or Lewis-acid catalysts is associated with a number of environmental problems [3,4]. A major drawback of such catalytic systems is that they cannot be regenerated, and for Friedel–Crafts acylation more than stoichiometric amounts of catalyst are needed. In addition to this, troublesome work-up steps are also necessary for treating the liberated hazardous and toxic waste products. To avoid major environmental hazards and to satisfy growing stringent global environmental regulations, it is imperative to develop a truly catalytic process with minimal waste production.

Consequently much attention has now been paid to simplifying the existing Friedel–Crafts process through the design of strong heterogeneous acid catalysts that can replace the conventional hazardous liquid- or traditional waste-generating Lewis-acid catalysts [5]. For many organic reactions involving nonbulky substrates and products, acidic zeolites are quite efficient. Although the acidity of zeolites is not as strong as that of anhydrous $AlCl_3$ or liquid mineral acids, they were found to be quite promising catalysts for acylation reactions of activated aromatic compounds such as toluene, xylenes, anisole, veratrole, or methoxynaphthalene [6–12].

On the other hand, sulfonic acid groups immobilized on solid supports like silica were found to catalyze many organic reactions [13,14]. In recent years this idea was further

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0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.01.007

developed for the design of hybrid organic–inorganic mesoporous silicas functionalized with alkylsulfonic acid groups [11,15–23]. These hybrid materials combine extremely high surface areas and larger and more tunable pore diameters than conventional zeolites. They exhibited very high activity for many liquid-phase acid-catalyzed reactions like carboxylic acid esterification [16,17], aromatic alkylation [23], and condensation reactions [16,21]. Covalent anchoring of the sulfonic acid functional groups to the silica surface by alkyl chain tethers could be achieved either by a direct synthesis route [15,17,19,20] or via an indirect postsynthetic anchoring technique [15,21] followed by an oxidation step to generate the sulfonic acid groups [15,21]. Recently we reported anchoring of Nafion-like perfluorinated sulfonic acid groups to mesoporous silica surfaces by a simple one-step method [24]. Nafion is one of the most versatile acid catalysts that contains terminal sulfonic acid groups attached to a perfluoroalkyl polymeric backbone [25,26]. The presence of electron-withdrawing fluorine atoms in the structure significantly increases the acid strength of the terminal sulfonic acid groups, which is quite comparable to that of pure sulfuric acid. However, as Nafion has a very low surface area and exhibits low catalytic activity, we show in this report that perfluoroalkylsulfonic acid chains anchored to MCM-41 give rise to catalysts that are very active for esterification of long-chain fatty acid with alcohols and for acylation of anisole with acetic anhydride. The activity of this hybrid organic–inorganic catalyst gives better performance than commercial Nafion silica catalysts or sulfonic groups anchored on mesoporous molecular sieves.

2. Experimental

2.1. Catalyst preparation

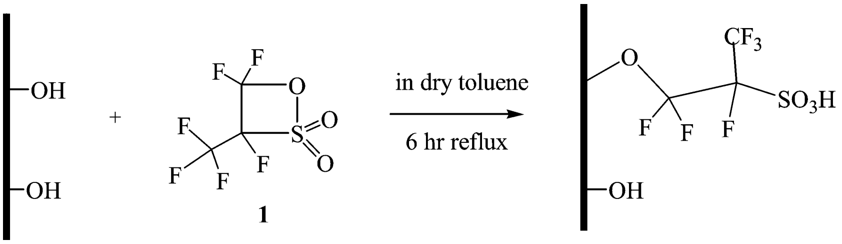
Purely siliceous MCM-41 was synthesized according to a method described in the literature [27]. MCM-41 silicas were functionalized with a 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid beta-sultone (**1**) (from ABCR chemicals) to obtain sulfonic acid groups anchored to the silanol groups with perfluoroalkyl tethers (Scheme 1). Calcined MCM-41 (2.0 g) was evacuated at 120 °C for 8 h and cooled to room temperature, and then a solution of **1** (1.0 g) in 50 ml dry toluene was added. The mixture was refluxed for 4–6 h under an inert atmosphere, and then the solid was filtered and washed thoroughly with toluene to remove any unreacted **1** or by-products. Finally the solid was dried at 100 °C overnight. We adjusted the amount of the organic loadings by varying the amounts of **1** in the treatment solution. For purposes of comparison, we also prepared one alkylsulfonic acid anchored on MCM-41 (MPS) according to the general method described in the literature [21] by first anchoring mercaptopropyl groups to MCM-41 silica and then oxidizing the thiol groups to sulfonic acid groups, with the use of a mild oxidation step. Commercial Nafion silica composite catalyst (SAC-13) was obtained from Aldrich.

2.2. Characterization

X-ray diffraction patterns of the ordered mesoporous silicas with the anchored perfluorinated sulfonic group were recorded with a Philips X'pert diffractometer operating at 40 kV and 35 mA, with the use of nickel filtered Cu-K_α radiation ($\lambda = 1.54178$ Å). Infrared spectra of the solids at various temperatures under vacuum were recorded in a Nicolet 710 spectrophotometer with the use of thin self-supporting wafers and mounted in a special high-temperature IR cell. The organic content of the solids was determined by combustion analysis in a Fisons EA 1108 elemental analyzer. Thermogravimetric analysis of the solids was performed in a Mettler 851 at a heating rate of 10 °C/min in an air stream. TG-MS analyses were carried out in a Perkin–Elmer TGA thermobalance coupled to a Fisons mass spectrometer. We measured specific surface area and pore size distribution of the solids by recording the nitrogen adsorption/desorption isotherms at liquid N_2 temperature (77 K), with the use of a Micromeritics ASAP 2000 system. Before measurements, the samples were outgassed at 150 °C under vacuum (10^{-3} Torr) for 6 h to remove any adsorbed species. Pore size distribution was determined from the desorption branch of the isotherm by the BJH (Barrett–Joyner–Halenda) method with the use of the Halsey equation. Solid-state ^{19}F MAS NMR spectra were recorded with a Bruker 400 spectrometer with samples packed in zirconia rotors spinning at 30 and 5.5 kHz, respectively.

2.3. Catalytic reactions

Catalytic reactions were carried out in the open air in a three-necked glass flask fitted with a cooling condenser and a heating bath. For esterification reactions, 2.0 mmol of the



Scheme 1.

Table 1
Physical properties of the hybrid catalysts

Sample	Amount of **1** (mmol) used per g of solid	S content of final solid (mmol/g)	S_{BET} (m^2/g)	V_p (cm^3/g)	C/S[a]
MCM-41	–	–	1030	0.95	–
MFS-1	0.5	0.16	912	0.90	2.9
MFS-2	1.0	0.22	745	0.87	3.0
MFS-3	1.5	0.45	680	0.74	2.9
SAC-13	–	10–20%[b]	> 200[b]	–	–
MPS	–	0.52	855	0.83	4.5

[a] From chemical analysis.
[b] From manufacturers data.

acid and an excess of alcohol (5 ml), if not otherwise mentioned, were used. The mixture was heated to the desired reaction temperatures, and then 50 mg of the dry catalyst was added and stirred continuously. Reaction products were collected at different time intervals, separated from solid catalyst particles by means of a syringe filter, and analyzed by gas chromatography (HP5890 with HP-5 column). For acylation reactions, 2.0 mmol of anisole and 2.0 mmol of acetic anhydride were introduced into the reactor and heated to the desired reaction temperature. Then 50 mg of the dry catalyst was introduced. We monitored the progress of the reaction by taking a small aliquot of the mixture and analysing it by gas chromatography as indicated above.

3. Results and discussion

The cyclic precursor 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid beta sultone (**1**) reacts with the silanol groups of the silica surface by opening up the sultone ring and forming a covalent bond between the silica framework and the perfluoroalkyl chain (see Scheme 1). Thus the silica surface becomes grafted to the perfluoroalkyl chains with a terminal sulfonic acid functional group. In contrast to the methods reported earlier for the preparation of anchored sulfonic acid silica catalysts, this new method is much simpler in the sense that in a single step, anchoring and formation of the sulfonic group are accomplished. Conventional methods require a subsequent thiol oxidation step after anchoring of the thiol-containing precursor molecules. Then a nonoptimized oxidation step generally leads to the formation of catalytically inactive disulfide species [15,16,21], and although optimized oxidation should lead to sulfonic acid, this has proved to be rather difficult in covalently attached mercapto groups. In our case, during the anchoring step the ratio of sultone **1** to mesoporous silica can be varied over a wide range (Table 1) to obtain different loadings of the perfluoroalkylsulfonic groups. Typically a 0.5–2 wt% sulfur loading can be obtained by adjustment of the amounts of **1** in the treatment solution.

XRD patterns for the solids (Fig. 1) were found to be very similar to those for the parent MCM-41 silica material, thus indicating that under the reaction conditions the long-range ordering of the mesoporous silica material was not affected by the anchoring of perfluoro-alkylsulfonic acid groups. However, attempts to load larger amounts (> 2 wt%) of perfluoroalkylsulfonic acid groups caused significant damage of the mesoporous structure, producing rather amorphous like material. This may be related to the presence of a high population of strong Brønsted acid sites formed during the covalent anchoring.

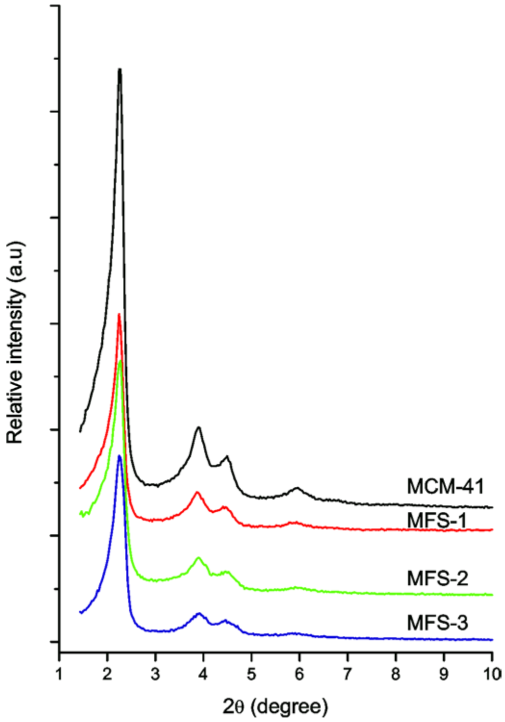


Fig. 1. XRD of MCM-41 and different MFS samples.

The amount of organic material loaded in the MCM-41 was determined by elemental analysis. For all samples the atomic ratio of carbon to sulfur was found to be very close to the theoretical value of 3. Thermogravimetric analysis of the hybrid materials showed an initial loss of weight (ca. 8%) up to 150 °C, which can be attributed to adsorbed water. This was followed by a second weight loss (ca. 3 wt%) step that extended to 350 °C. The observed weight loss between 150 and 350 °C is relatively minor in comparison with that observed for MCM-41 silica functionalized with n-propyl-tethered sulfonic acid groups. In the latter case, loss of the organics was almost complete in this temperature range [28], whereas in the case of the MFS materials prepared here, most of the weight loss (depending on the perfluoroalkylsulfonic group loading) occurs at temperatures higher than 350 °C. This thermogravimetric analysis shows the higher thermal stability of our perfluoroalkylsulfonic MCM-41. To further confirm the thermal stability of the perfluoroalkylsulfonic groups, thermal analysis coupled with mass spectroscopy was performed. Mass spectrometric data revealed that up to 350 °C mostly water molecules were desorbed from the solids. A small amount of SO_2 was also detectable, but only above 350 °C [24].

The nitrogen adsorption–desorption isotherms of the solids show Type IV curves according to the IUPAC nomenclature, indicating the mesoporous nature of the solids. A typical isotherm is shown in Fig. 2. The BET surface area and pore volume of the samples are given in Table 1. It can be seen that the specific surface area and pore volume decreased continuously with higher loading of the organics. Also it was noted that the pore size distribution measurements showed a slight decrease and broadening of the average pore diameter with the anchoring of the organics.

The presence of sulfonic acid groups can be observed from the FT-IR spectra of the self-supporting wafers of the solids. The band at 1420 cm^{-1} (Fig. 3) is characteristic of $\nu_{S=O}$ stretching vibrations of undissociated $–SO_3H$ groups as reported previously for Nafion films and triflic acid [29,30]. Strong binding of the perfluoroalkylsulfonic acid groups to the surface of the mesoporous silicas and thus the increased thermal stability were also reflected by the preservation of the strong intensity of this band even at elevated outgassing temperatures. Other bands observed at 1650 and 1760 cm^{-1} were assigned to the vibrations of adsorbed and protonated water molecules respectively, as reported by other workers in IR studies on Nafion [29,30]. As a matter of fact, upon degassing at increasing temperatures, these bands undergo some shift to higher wavenumbers and a decrease in intensity until they become very weak. This decrease in intensity of the bands attributable to protonated water varies independently of the band corresponding to the $–SO_3H$ group.

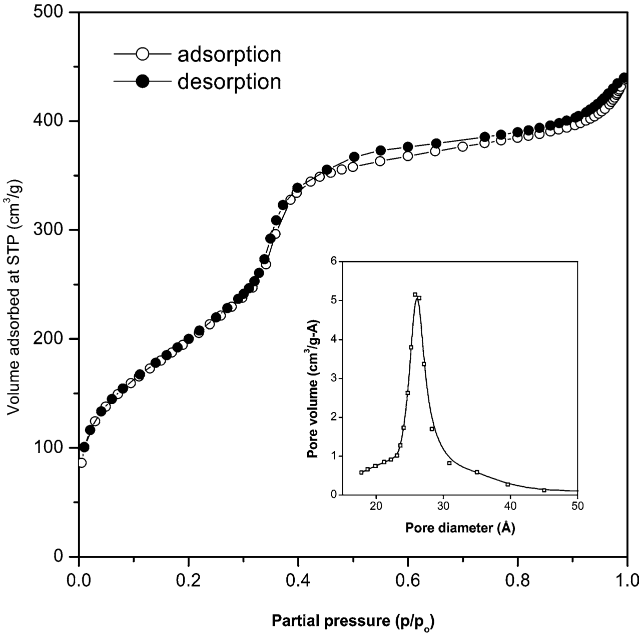


Fig. 2. Adsorption–desorption isotherm and pore size distribution (inset) of MFS-2 sample.

Covalent attachment of the perfluoroalkylsulfonic acid chains to the silica surface was also confirmed by ^{19}F MAS NMR experiments. Fig. 4 shows a MAS ^{19}F NMR spectrum for a typical solid. Three separate peaks were observed in accordance with the presence of three different environments of the F atoms. Peaks around −164 and −157 ppm can be assigned to F atoms from C–F and $C–CF_2$ moieties. In contrast, the signal for CF_3 group appeared markedly downfield at −74 ppm. Integration of the signal peaks showed the ratio of the peaks to be close to 1:3:2, which is in full agreement with the theoretical value. We notice that the peak attributable to CF_2 appears as a very broad signal as compared with the other two peaks. This broadness could be due to a distribution of groups with different environments or to anisotropy or some other inhomogeneity arising from the immobilization on the solid surface. While in solution the chemical shift of the CF_3 corresponding to the Beta-sultone appearing at −76 ppm is similar to the value measured for the solid; the chemical shifts corresponding to the CF and CF_2 of Beta

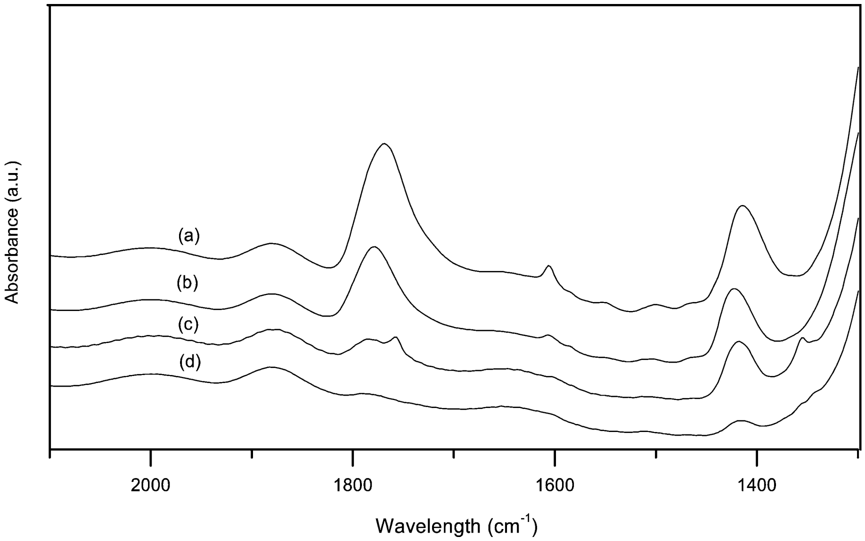


Fig. 3. FT-IR spectra of MFS-2 sample at different temperatures (a) 30, (b) 100, (c) 200, and (d) 300 °C.

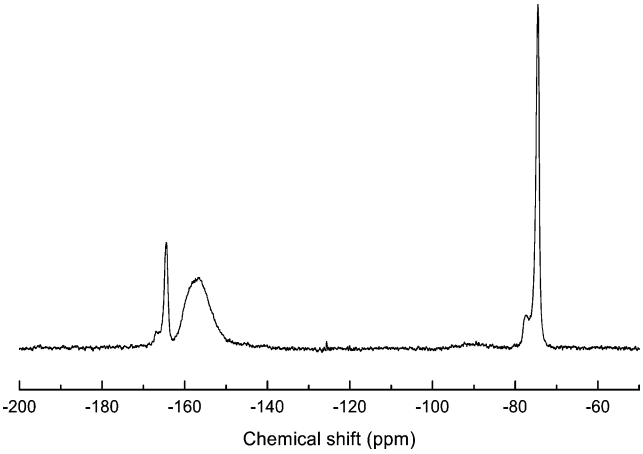


Fig. 4. ^{19}F MAS NMR of MFS-2 sample.

sultone appear at −84 and −90 ppm and are notably shifted with respect to the perfluoro chains in the solids.

Although the initial covalent attachment of the perfluoroalkylsulfonic groups on the mesoporous MCM-41 structure appears to have been firmly demonstrated, a point that deserves further study is the persistent tendency of this bond to undergo hydrolysis under catalytic conditions.

3.1. *Esterification of alcohols*

The catalytic performance of the hybrid MCM-41 materials was tested for the esterification of long-chain aliphatic acids with alcohols at ambient atmosphere. The catalysts are very active for the esterification of C_8 and C_{12} aliphatic acids with alcohols like ethanol and dodecanol (Table 2). In the case of octanoic acid esterification with ethanol, the conversion of acid reached 95–96% within 6 h at a relatively low temperature of 60 °C. Although blank controls revealed that the esterification reaction also proceeds in the absence of any solid catalyst, the reaction was comparatively considerably slower.

Table 2
Esterification of alcohols with fatty acids[a]

Substrate	Acid	Solvent	*T* (°C)	Conversion (%)
Ethanol	Octanoic acid	Ethanol excess	60	99
Ethanol	Dodecanoic acid	Ethanol excess	60	61
Ethanol	Dodecanoic acid	Ethanol excess	80	81
Dodecanol	Octanoic acid	Toluene	60	58
Dodecanol	Octanoic acid	Toluene	80	98
Dodecanol	Dodecanoic acid	Toluene	60	60
Dodecanol	Dodecanoic acid	Toluene	80	90

[a] Catalyst MFS-3, reaction time 24 h.

The activity per gram of hybrid mesoporous silica catalysts is almost double that of the commercial Nafion silica composite SAC-13 [24]. On the other hand, the turnover frequency (activity per sulfonic acid group) was one order of magnitude higher for the hybrid catalysts (9.7×10^{-3} s^{-1}) than for commercial SAC-13 catalyst (1.1×10^{-3} s^{-1}). Since commercial SAC-13 has a higher density of sulfonic groups than do the hybrid catalysts, we have to conclude that the accessibility of sulfonic groups is higher in our hybrid MCM-41 catalyst and/or the interactions of sulfonic acid groups with the surface silanol groups of the silica matrix in SAC-13 catalysts decrease its acidity and therefore its catalytic activity. It is obvious that as the reaction progresses the formation of water as a by-product will cause the acid strength of the Brønsted sites to level off; therefore, it appears that accessibility may be the key factor responsible for the relative catalytic activity.

Fig. 5 shows the time conversion plots for three different catalysts, namely hybrid MFS-3, MPS, and SAC-13, for the esterification of octanoic acid with ethanol at 60 °C. It can be seen there that the activity per gram of our perfluoroalkylsulfonic MCM-41 catalyst MFS-3 is also much higher than the

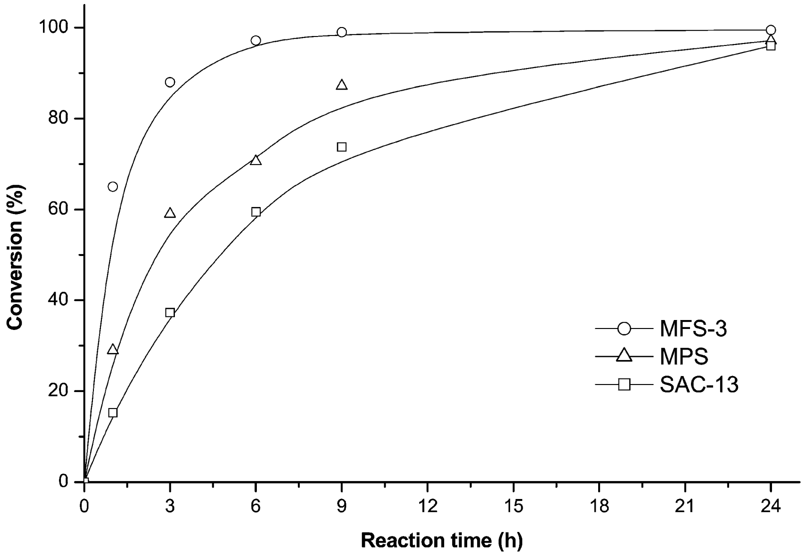


Fig. 5. Time–conversion curves for esterification of octanoic acid with ethanol at 60 °C with different MFS catalysts and SAC-13.

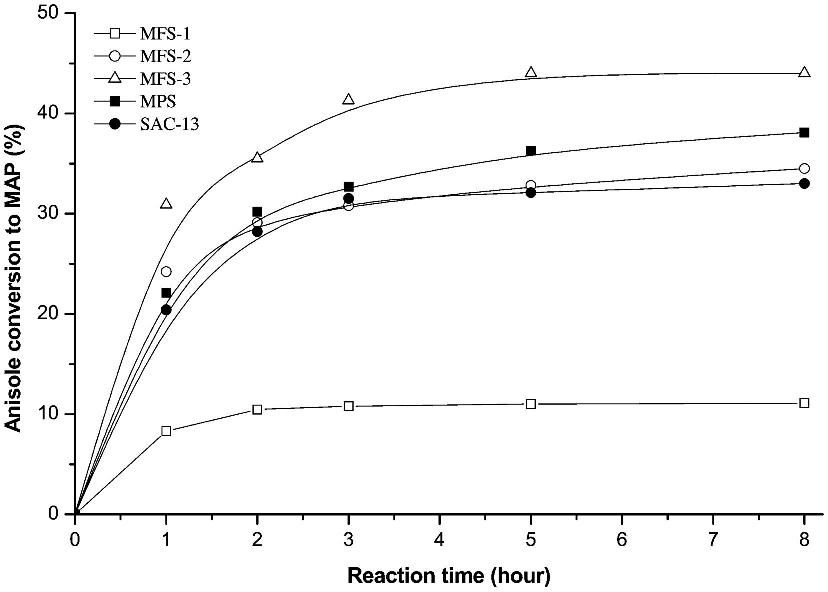


Fig. 6. Time–conversion curves for acylation of anisole with acetic anhydride at 60 °C with different MFS catalysts and SAC-13.

corresponding alkylsulfonic acid MCM-41 (MPS). This is a reflection of the expected influence of perfluorination on the acidity and catalytic activity of the sulfonic acid group. After recovery of the solid and washings with ethanol, MFS-3 was reused six times under the same conditions with only a minor decrease (15%) in activity between the first and the second run; the self-esterification was still much lower when it was uncatalyzed than when it was catalyzed.

It was noticed that with longer chain fatty acids and higher alcohols the reaction proceeded more slowly and an increase in the reaction temperature had a favorable effect on the conversion (see Table 2). The selectivity for the corresponding esters was always very high, with almost no side-product formation. Mass balances were also high and, therefore, ester yields correspond very well with the acid conversions indicated in Table 2. Reactions performed in the absence of any catalyst or in the presence of only siliceous MCM-41 support showed negligible conversion of the acids, indicating the truly catalytic nature of the reaction. In addition, we found the catalyst to be reusable by washing with ethanol after the reaction, with an initial slight loss in activity after the first run.

3.2. Acylation of anisole

Acylation of anisole was also carried out with acetic anhydride in the presence of hybrid MCM-41 catalysts. Earlier work reported acylation of anisole with various heterogeneous catalysts like Ce-exchanged clays [31], $FeCl_3$- or $ZnCl_2$-impregnated clays [32], and heteropoly acid catalysts [33–35]. Zeolite catalysts like Beta [9], Y [6,8,10], and ZSM-5 [12] were also reported to be quite active for the acylation of activated aromatic compounds. Nafion silica composite catalysts were also reported to be active for the acylation of anisole with acid chlorides [36]. However, we preferred to avoid halogen-containing acid chlorides, and instead acetic anhydride was used as an acylating agent. Although cesium-containing heteropoly acids have been reported to be able to acylate anisole with aliphatic acids [34], our attempts to acylate anisole with aliphatic acids in the presence of Nafion MCM-41 or SAC-13 catalysts were not successful.

Fig. 6 shows the time anisole conversion plot at 60 °C, where MFS catalysts have different S loadings. As expected, the activity increases directly with the sulfur content. Furthermore, the turnover number is 2.5 times lower for either nonfluorinated MPS or commercial SAC-13. The selectivity for the desired para isomer, 4-methoxyacetophenone, was almost 97% for the three catalysts, and only a very small amount of 2-methoxyacetophenone was observed.

An increase in reaction temperature has a beneficial effect on the conversion of anisole to methoxyacetophenone and on the yield of 4-methoxyacetophenone. This is quite expected, and similar effects were observed for Nafion silica composite catalysts [36]. Fig. 7 shows the effect of reaction temperature on the anisole conversion. 4-Methoxyacetophenone yields follow analogous behavior. It has been observed that at lower temperatures, conversion increased rather slowly with time and reached the final value only after 3 h. However, at elevated temperatures the maximum conversion was reached very quickly within 1 h, and after that there was a very slight increase in conversion with time. From the shape of the conversion curves it is clear that MFS catalysts become deactivated during the acylation reaction.

I has been reported that in the case of zeolite catalysts the activity of the acylation catalyst can be recovered by regeneration [9,11]. It was also possible to bring about the regeneration of heteropoly acid catalysts through cleaning of the spent catalysts [33]. However, strong adsorption of carbocationic compounds on the active sites can deactivate the cat-

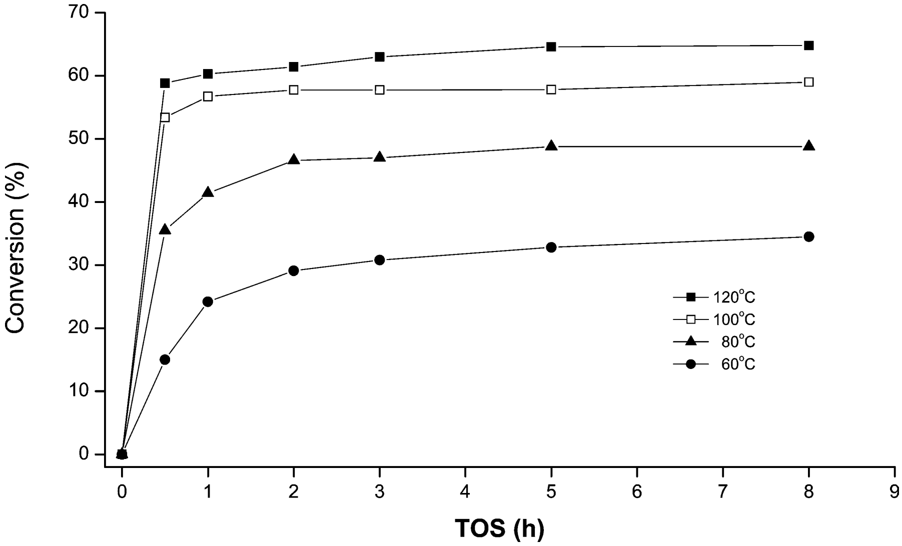
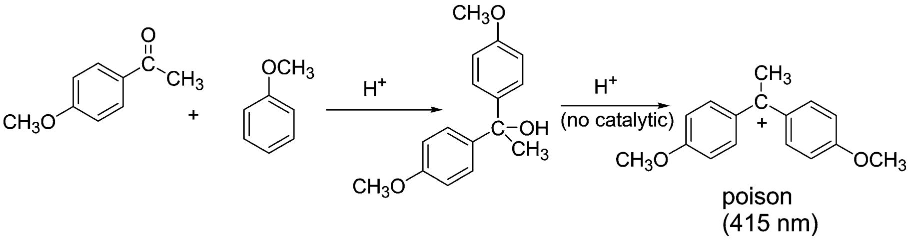


Fig. 7. Time–conversion curves for acylation of anisole with acetic anhydride at different reaction temperatures with MFS-2 catalysts.



Scheme 2.

alyst easily. Although activity of the perfluorosulfonic acid-anchored MCM-41 catalysts can be regenerated after esterification reaction by washing with ethanol, in the acylation reactions the activity of the fresh fluorinated MFS cannot be regenerated. This may be due to strong adsorption of some species on the active sites. Indeed, the diffuse reflectance UV–vis spectrum of the used catalysts showed a strong peak around 415 nm, indicating the presence of adsorbed species on the catalyst surface. Carbocationic intermediates are the most likely poisons at this stage, in view of the precedents in the literature [37,38]. These species are found to be generated by secondary reactions of 4-methoxyacetophenone, as indicated in Scheme 2.

4. Conclusions

Hybrid organic–inorganic Nafion-MCM-41 silicas represent a promising type of catalyst for acid-catalyzed reactions. Anchoring of perfluorinated alkylsulfonic groups to the high-surface-area MCM-41 silica can be achieved in a single step and produces strong solid acid catalysts that are stable up to 350 °C. The esterification of long-chain fatty acids can be performed satisfactorily at a relatively low temperatures with high yields of the desired esters. The perfluoroalkylsulfonic MCM-41 catalyst can be reused after recovery and washing. Furthermore, acylation of anisole can be carried out with good conversion and a very high selectivity for the desired para isomer, although deactivation by diaryl carbocations limits at present the reusability of the system. For both reactions the new "Nafion" MCM-41 catalysts exhibit significantly higher activity than any of the previously reported hybrid inorganic–organic acid catalysts. Further studies are needed to establish the stability of this covalent bond during hydrolysis under strong acid conditions and the influence of the presence of residual silanol groups in the acid strength of the perfluoroalkylsulfonic groups.

Acknowledgments

Financial support by the Spanish Ministry of Science and Technology (MAT2003-1767) is gratefully acknowledged. D.D. thanks the Generalidad Valenciana for a fellowship.

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