Electronic Supporting Information

Size and ability do matter!

Influence of acidity and pore size on the synthesis of hindered halogenated meso-phenyl porphyrins catalysed by porous solid oxides

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1. Materials and methods

All starting materials (aryldehydes and pyrrole) were bought from Aldrich, having the highest grade available and used as received. Solvents were purified by standard methods.[1] Zeolite NaY was purchased from Zeolyst, mesoporous Al-MCM-41 was purchased from Aldrich.

Al-SBA-15 and Si-MCM-41 materials were synthesized according to previously given procedures.[2] Si-SBA-15 material was synthesized as follows: first 10.5 g of triblock copolymer (Pluronic P123, Aldrich) was dissolved in 405 ml of water under magnetic stirring, overnight; after that, an aqueous solution of HCl (2M), 23.8 g of TEOS (Aldrich) and 10 g of NaCl (Fluka) were successively added and the final solution heated at 40 ºC for 24 h; the mixture obtained was finally transferred into a polypropylene bottle and heated at 100 ºC during 72 h; the product was centrifuged, washed with distilled water and dried at 80 ºC overnight. All the materials synthesized were calcined at 550 ºC under air for 10 h, in order to remove the organic template.

All synthesized porphyrins were compared with samples prepared using the nitrobenzene method.[3] The porphyrins prepared here are meso-tetra(2-fluorophenyl)porphyrin (TFPP), meso-tetra(2,6-difluorophenyl)porphyrin (TDFPP), meso-tetra(pentaflurophenyl)porphyrin (TPFPP) and meso-tetra(2,6-dichlorophenyl)porphyrin (TDCPP). Column chromatography was performed using silica gel (from Aldrich, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size) as stationary phase; porphyrin structures were confirmed by ^{1}H-NMR, and are in accordance with the literature.

2. Instrumentation

A Bruker 400 MHz spectrometer was used to measure ^{1}H-NMR spectra in deuterated chloroform, using TMS as internal standard. UV–vis absorption spectra of solution samples were measured on a Shimadzu UV-2010 double-beam spectrometer over the range 200–800 nm. DRS-UV–vis absorption spectra of solid samples were recorded on a Shimadzu UV-2450 double-beam spectrometer with an integrating sphere over the range 300–800 nm, using $BaSO_4$ as reference. Luminescence spectra were obtained on a SPEX Fluorolog 3-22 spectrophotometer, using a 300 W xenon arc lamp as excitation source. The luminescence spectra on solid samples were measured using a specially designed metal support with a quartz window. Thermogravimetric analyses were made in air using a TG-DSC Setsys Evo16 instrument (Setaram) with a heating rate of 10 °C/min to a maximum temperature of 1000 °C.

3. Characterization of acidic properties of catalytic supports

Acidity measurements were performed using pyridine as probe molecule, followed by Infrared spectroscopy (FTIR); a Nicolet Nexus spectrometer was used for the purpose. In a typical experiment, samples were pressed into thin wafers (10-20 mg/cm^2) and heated in an IR glass cell from room temperature up to 300 ºC (mesoporous materials) and 450 ºC (zeolite) (5 ºC.min^{-1}) for 3 h under vacuum (10^{-5} mbar). Afterwards, the samples were cooled down to 150 °C and left in contact with pyridine for 10 min. Then, excess probe molecule was removed for 30 min under vacuum and the IR spectra were recorded; 64 scans with a resolution of 4 cm^{-1} were collected for each spectrum. The concentrations of Brönsted and Lewis sites able to retain the pyridine at 150 ºC were determined using the integrated areas of the bands at 1541 cm^{-1} and 1454 cm^{-1}, (1445 cm^{-1} for NaY sample),[4] respectively, and the extinction coefficients determined by Emeis (Fig. 1).[5]

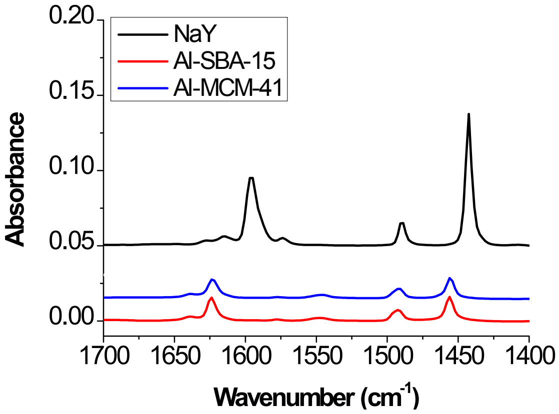

Fig. 1 FTIR spectra (difference) of the different catalysts obtained after pyridine contact and subsequent desorption under vacuum at 150 ºC for 30 min

4. Thermal analysis

Samples were characterised using TG/DSC method, in temperature range 25-800 ºC (10 ºC/min) (TG-DSC Setsys Evo 16 equipment, Setaram). The curves obtained for thermal behaviour of solids immobilised in the mesoporous materials are represented in Fig. 2.

The weight loss in samples of 1a–1e occurs in three steps: below 100 ºC, 200–420 ºC, and above 420 ºC. The first step (T<100 ºC) can be assigned to desorption of volatile solvents and water molecules which are physically adsorbed in the samples. The second step can be related to decomposition of porphyrins and organic groups. The weight loss above 420 ºC can be attributed to the further oxidation of the remaining organic compounds and, to a less extent, dehydroxylation of silanol groups. These results indicate that the hybrids of silica porphyrins show relatively high thermal stability.

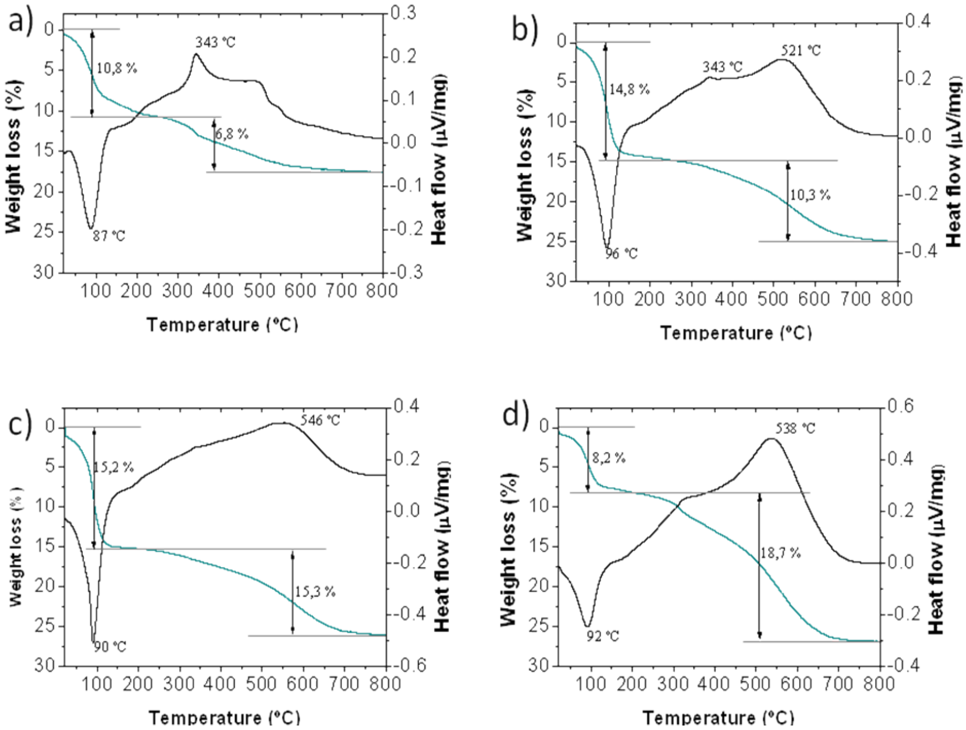

Fig. 2. TG/DSC curves: a) TDFPP@Si-SBA-15; b) TDFPP@Si-MCM-41; c) TDFPP@Al-SBA-15 and d) TDFPP@Al-MCM-41; ▬ weight loss (%) and ▬ heat flow (µV/mg) as temperature function.

When the mesoporous materials used were Si-SBA-15 and Si-MCM-41, the weight loss was about 6.8 and 10.3 %, respectively, while for Al-SBA-15 and Al-MCM-41 was 15.3 and 18.7 %, respectively. It can be concluded that the mesoporous material that possesses both Al and the smaller pore size (Al-MCM-41) allows the highest amount of TDFPP to be immobilised inside its pores.

Table 1. Values for weight loss and heat flux maximum temperature peaks.

SAMPLE	Weight loss (%)		DSC peaks (º C)		
	25-100 °C	200-800 °C	I (endo)	I (exo)	II (exo)
TDFPP@Si-SBA-15	10.8	6.8	87	343	
TDFPP@Si-MCM-41	14.8	10.3	96	343	521
TDFPP@Al-SBA-15	15.2	15.3	90	546	
TDFPP@Al-MCM-41	8.2	18.7	92	538	

5. Typical assisted synthesis of porphyrins with the acid catalysts

In a typical experiment, 0.5 g of catalyst was introduced into a 50 mL round flask, previously filled with a glacial acetic acid/nitrobenzene mixture (9.5 mL/7.4 mL) and aryldehyde (1.25 mmol). Addition of equimolar amount of pyrrole (1.25 mmol) was carried out dropwise under stirring and heating of the suspension (≈120 °C). After complete addition, the suspension was heated further to attain the reflux temperature (≈130 °C) and maintained at this temperature for *ca.* 2 hours. The hot suspension was filtered and the resulting solid material washed with chloroform and tetrahydrofuran until no coloured material was collected on the supernatant. The volume of supernatant was then reduced by rotoevaporation (enough volume to remove the added washing solvents). To induce porphyrin precipitation, methanol (*ca.*100 mL) was added in the cases of TFPP, and TDFPP and TDCPP. In the case of TPFPP, *n*-hexane (*ca.* 200 mL) was added. The Erlenmeyer flask containing the corresponding porphyrin was left in the refrigerator overnight and the deposited solid was collected by filtration and then purified by column chromatography (silica gel). The eluted solution was evaporated to dryness and the resulting crystals were dried under vacuum and weighed in a microbalance.

5.2. Porphyrin yield as function of the amount of support used

When reaction were performed using 1 g NaY/2.5 mmol 2,6-difluorobenzaldehyde, the yield obtained was *ca.* 22 %, with 0.5 g NaY/1.25 mmol 2,6-difluorobenzaldehyde, the yield obtained was *ca.* 23 %, with 0.25 g NaY/0.625 mmol 2,6-difluorobenzaldehyde, the yield obtained was *ca.* 20 %, and with 0.125 g NaY/0.312 mmol 2,6-difluorobenzaldehyde, the yield obtained was *ca.* 16 %. The results are compiled in Fig. 3 for TFPP and TDFPP.

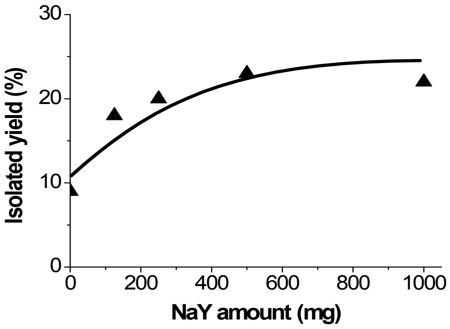

Fig. 3. Isolated yields of TDFPP *vs* NaY amount. Note: when amount NaY = 0, it represents the isolated yields using the nitrobenzene method.

5.3. Soxhlet extraction of filtered solids

The solid obtained after filtration of the suspension and washed with chloroform and tetrahydrofuran, to eliminate adsorbed compounds on the external surface, then the solid was further Soxhlet extracted sequentially with CH_2Cl_2, CH_3CN, C_2H_5OH and $CHCl_3$, until no porphyrin and/or precursors were detected in the solution. The resulting immobilized porphyrins were dried overnight at 150 °C, under vacuum.

6. Electronic spectral data for ground and excited state for TDFPP (chosen as model compound)

Samples were characterised using two spectroscopic methods, diffuse reflectance spectroscopy (DRS-UV-vis) and luminescence, in the wavelength range 200-800 nm. The DRS-UV-vis spectra are presented in Fig. 2 and show the influence of Al ions (Brönsted sites) and pore size in the immobilization of porphyrins. The DRS of TDFPP-Al-MCM-41 and TDFPP-Al-SBA-15 show intense bands at about 415 nm, typical of the Soret band of the DRS absorption spectra of pristine porphyrin. The low intensity of the Q bands may possibly result from the effect of light scattering. In contrast, with NaY as solid support, the broad band centred at 550 nm is attributed to the formation of the porphyrin precursor, FDPM, synthesized by direct condensation of benzaldehyde in pure pyrrole. This is in good agreement with a previous study described by Garcia *et al.*.[6] Table 2 includes the maxima of all bands present in Fig. 4.

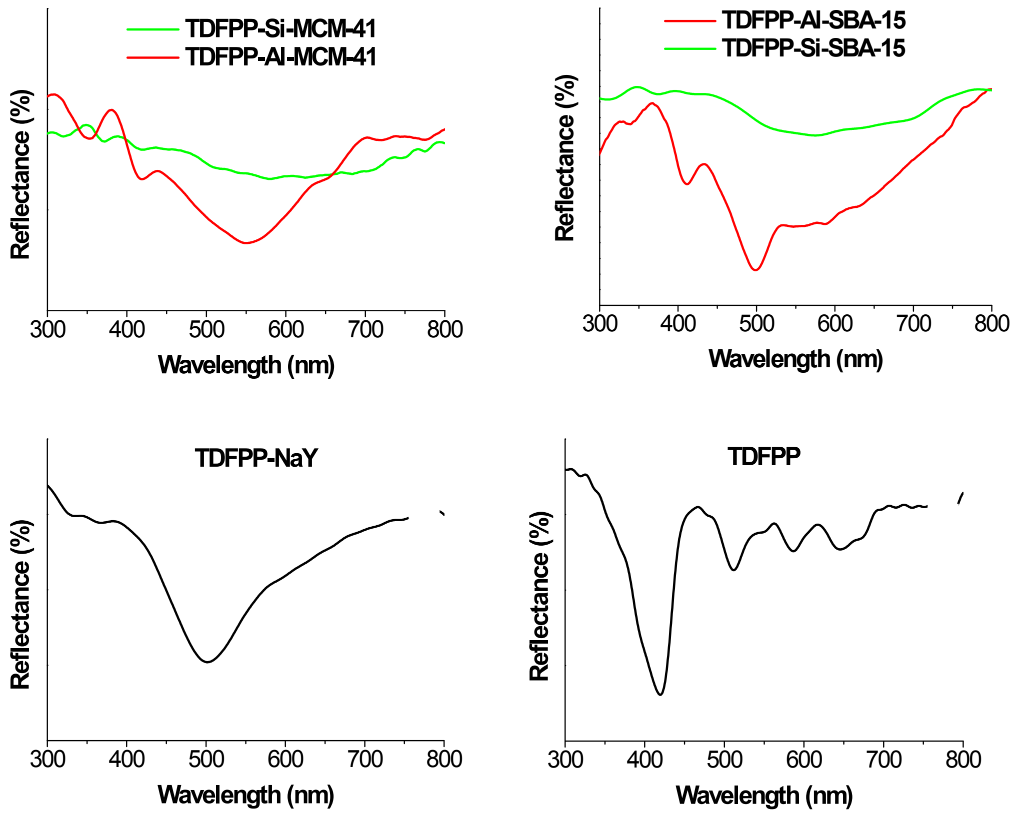

Fig. 4. Reflectance spectra of recovered solids after extraction and absorption spectrum of TDFPP.

Table 2. Maxima values in the electronic spectra of fundamental state for the recovered solids after extraction and isolation (TDFPP)

SAMPLE	λ_{max} (nm)
TDFPP-NaY	502.0; 588.0
TDFPP-Al-MCM-41	427.0; 508.0; 575.0; 659.0
TDFPP-Si-MCM-41	421.0; 510.0; 580.0; 658.0
TDFPP-Al-SBA-15	412.0; 499.0; 550.0; 645.0
TDFPP-Si-SBA-15	417.0; 509.0; 575.0; 655.0
TDFPP	420.0; 511.5; 586.5; 645.5

The emission spectra of the samples are presented in Fig. 5. The shape of the TDFPP-Al-MCM-41, TDFPP-Si-MCM-41, TDFPP-Al-SBA-15 and TDFPP-Si-SBA-15 spectra are in general agreement with that observed for TDFPP in CH_2Cl_2. The emission spectrum of TDFPP-NaY shows a broad band with maximum at 600 nm.

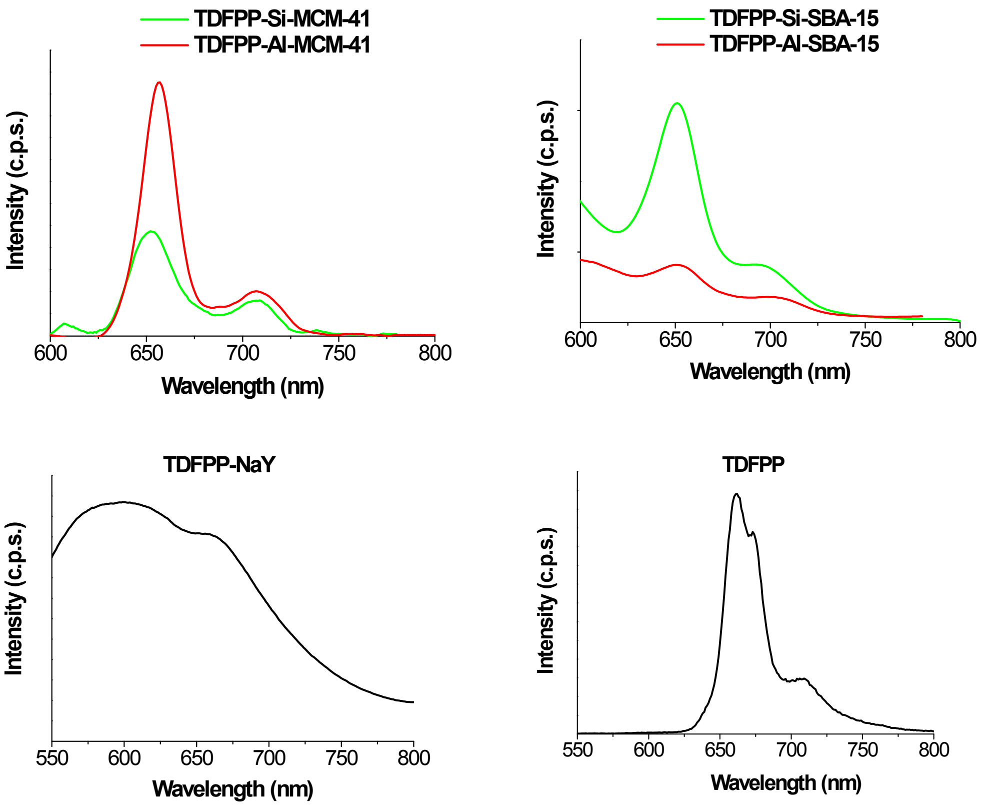

Fig. 5. Luminescence spectra of recovered solids after extraction and isolation (TDFPP).

7. Catalyst recycling

As zeolite NaY was chosen as the best support to assist the synthesis of porphyrins, the catalyst was tested in successive cycles to evaluate the reutilization process in the synthesis of TDFPP.

After the first cycle, the selected catalyst was collected by filtration and washed with chloroform and tetrahydrofuran, following drying of the solid overnight, at 150 ºC under vacuum. The second, third, fourth and fifth cycles were carried out with the recovered solid and reactivation procedure was followed for each reutilisation.

TG/DSC method was also used to characterise the immobilised solids on zeolite NaY, in the temperature range 25-800 ºC (heating rate 10 ºC/min) (Fig. 6).

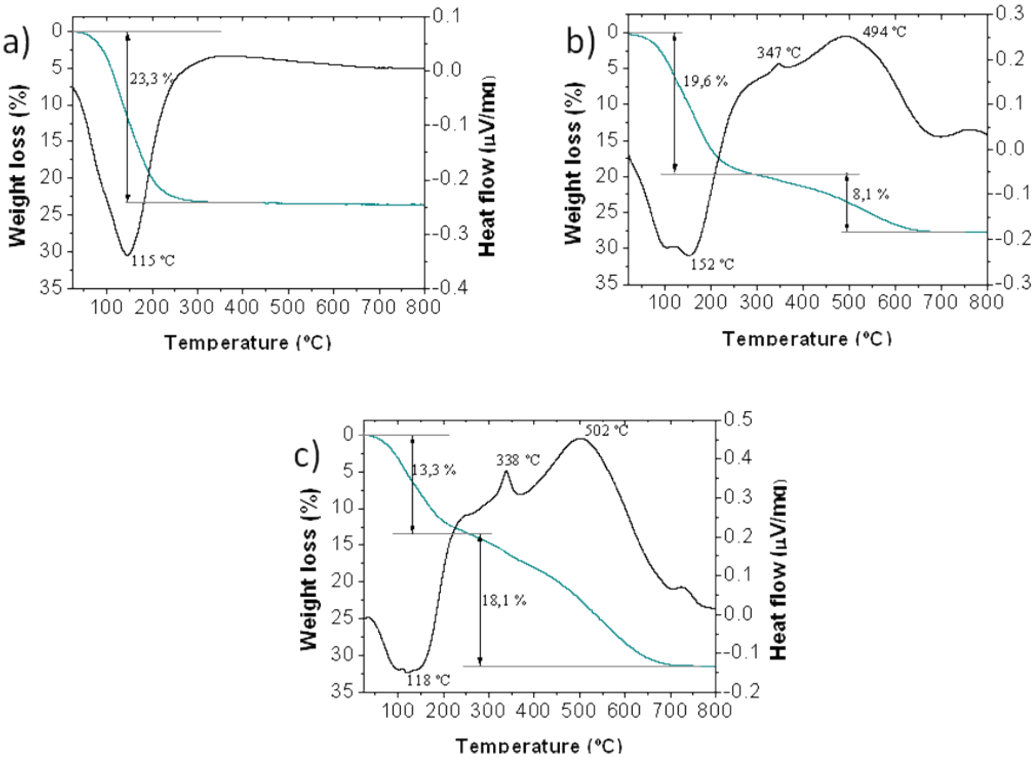

Fig. 6. TG/DSC curves for TDFPP synthesis in presence of NaY: (a) NaY pristine, b) TDFPP-NaY (after one cycle) and c) TDFPP-NaY (after 5 cycle reutilisation); ▬ weight loss (%) and ▬ heat flow as temperature function.

From this figure, it can be seen that, when NaY is used as “immobiliser”/catalyst, the weight loss values for water desorption are in the range of 23.3 % for pristine NaY, 19.6 % after one utilisation and 13.3 % after five reutilisations. As observed by UV-vis and luminescence studies, instead of having TDFPP inside the zeolite pores, the NaY, with the utilisation and reutilisation accumulates the reaction intermediates inside its pores, causing a gradual substitution of adsorbed water molecules by other molecules, as intermediates for the reaction, as well as their own accumulation inside the cavities of the zeolite.

Table 3. Values for weight loss and heat flow maximum temperature peaks.

SAMPLE	Weight loss (%)		DSC peaks (º C)		
	25-100 °C	200-800 °C	I (endo)	I (exo)	II (exo)
NaY	23.3		114		
TDFPP-NaY	19.6	8.1	152	347	494
TDFPP-NaY (after 5 cycles reutilisation)	13.3	18.1	118	338	502

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