Electronic Supplementary Material (ESI) for RSC Advances.

Determination of Total Organic Carbon on Hybrid Organic-Inorganic Mesoporous Silica by FT-NIR spectroscopy

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Supplementary Information

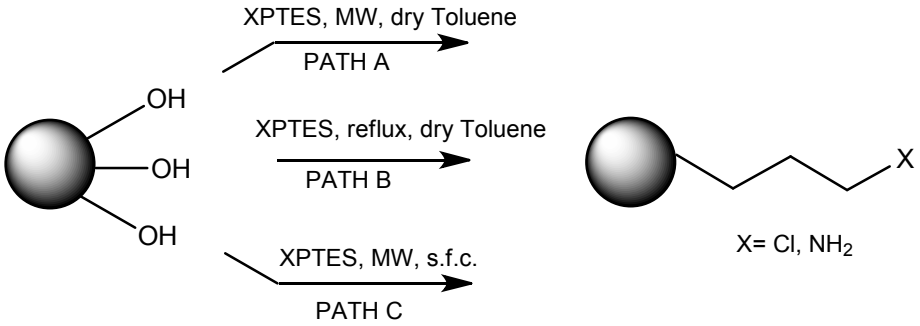
Table of Contents

Experimental

TOC measurements were carried out using an Analytic Jena multi N/C 2100 analyzer equipped with a HT 1300 oven. NIR measurements were performed in the reflectance mode using the Antaris II FT-NIR spectrophotometer (Thermo Scientific, Madison, WI, USA) equipped with an integrating sphere module. Each spectrum was the average of 64 scans, resolution was 4 cm -1 e transmission 0.5mm. The software used to collect the spectra and data processing was Thermo Scientific TQ Analyst (Thermo Scientific, Madison, WI, USA).

The MW reactions were performed into the microwave reactor Synthos 3000 by Anton Paar, equipped with a rotor 64MG5 and a IR sensor as temperature external control working in P-controlled mode; a conversion factor of 1.214 was applied to calculate the value of internal temperature. Reactions were performed in 0.3-3 ml glass vials closed with a PTFE seal and a screw-cup in PEEK. Reaction was controlled by TLC using silica plates 60-F264 on alumina, commercially available from Merck. TLC were performed using silica plates 60-F264 on alumina, commercially available from Merk. All solvents were distilled before using by standard methods. All chemicals were used as commercially available.

Syntesis of the MCM-41 hybrid samples



Scheme 1: General pathway of MCM-41 functionalization by a MW-assisted-Toluene method (Path A), a classical method (Path B) and a MW-assisted-s.f.c. method (Path C) at different times.

Pre-treatment of MCM-41 silica

1 g of MCM-41 was treated with 25 ml of an aqueous solution of HCl 5, 15 or 25% v/v for 3 hours at reflux temperature. The temperature was lowered until room temperature and the mixture was filtered. Solid was washed with water and dried overnight at 100°C.

Functionalization MW-assisted of MCM-41 with solvent (Path A, CS01-04, CS06-09, CS13-14, CS18-30, CS32-43, VS01, VS05-13)

Pre-treated MCM-41 (200 mg), suspended in 2.0 ml of Toluene dry, was reacted with 3-(chloropropyl)triethoxysilane (1 ml) for 5 up to 30 minutes in a sealed 2.0-5.0 ml vial equipped with a stirring bar of a MW-oven. The temperature was fixed at 110°C, 130°C, 150 °C or 170°C and it was continuously controlled by an external IR controller. At the end of the reaction the system was cooled until room temperature. The solid was filtered, washed three times with THF and extracted for 2 hours in CH_2Cl_2/Et_2O mixture using a Soxhlet extractor, then dried under vacuum and stored overnight at 70°C. The functionalized mesoporous material obtained was stored under dried conditions.

Functionalization of MCM-41 using classical heating (Path B, CS05, CS31, CS44-49, VS02-03, VS14)

Pre-treated MCM-41 (200 mg) suspended in 2.0 ml of Toluene dry was reacted with 3-(chloropropyl)triethoxysilane (1 ml) for 3 hours up overnight in a two-neck round-bottom flask equipped with a stirring bar and a condenser, at the reflux temperature of the solvent. At the end of the reaction the system was cooled until room temperature. The solid was filtered, washed three times with THF and extracted for 2 hours in CH_2Cl_2/Et_2O mixture using a Soxhlet extractor, then dried under vacuum and stored overnight at 70°C. The functionalized mesoporous material obtained was stored under dried conditions.

Functionalization MW-assisted- solvent free conditions of MCM-41 (Path C, CS10-12, VS04, VS15)

Pre-treated MCM-41 (200 mg) was reacted with 3-(chloropropyl)triethoxysilane (1 ml) for 5 up to 30 minutes in a sealed 2.0-5.0 ml vial equipped with a stirring bar of a MW-oven. The temperature was fixed at 110°C, 130°C, 150 °C or 170°C and it was continuously controlled by an external IR controller. At the end of the reaction the system was cooled until room temperature. The solid was filtered, washed three times with THF and extracted for 2 hours in CH_2Cl_2/Et_2O mixture using a Soxhlet extractor, then dried under vacuum and stored overnight at 70°C. The functionalized mesoporous material obtained was stored under dried conditions.

Functionalization of MCM-41 in sealed oil bath (CS15-17)

Pre-treated MCM-41 (200 mg), suspended in 2.0 ml of Toluene dry, was reacted with 3-(chloropropyl)triethoxysilane (1 ml) for in a sealed 2.0-5.0 ml vial equipped with a screw cap and an internal fibber optic as temperature control, under high stirring (400 r.p.m.) in an oil bath warmed at the fixed temperature of 145°C. The internal temperature of 130°C was reached in 2 minutes and the mixture was allowed to react at this temperature for 10 min. At the end of the reaction the system was cooled until room temperature. The solid was filtered, washed three times with THF and extracted for 2 hours in CH_2Cl_2/Et_2O mixture using a Soxhlet extractor, then dried under vacuum and stored overnight at 70°C. The functionalized mesoporous material obtained was stored under dried conditions.

TOC accuracy

TOC accuracy measurement was performed on two different silica samples (CS42, CS43) characterized by two different loadings near to the average loading.
Ten measures were performed on each sample in order to assess the uncertainty related to repeatability.
The expanded uncertainty U_e was calculated by the following equation:

$$Ue = k_p \cdot \mathring{U}_c(y) \cdot y$$

Where

k_p is the coverage factor, calculated on the basis of the desired level of confidence (95%) and the effective freedom degrees number (ν_{eff}) for each uncertainty contribution. K_p were calculated according to the Table DT-0002 of the ACCREDIA guide

$\mathring{U}_c$ is the combined uncertainty related, composed by the contribution of the uncertainty related to the repeatability, the uncertainty related to the instrument calibration and the uncertainty related to weighing

y is the measure

The TOC accuracy determined was 30%.

Calibration set table

Table 1. TOC values (mmol C/gr of catalyst) of mesoporous silica samples, used for calibration, functionalized by a MW-assisted-Toluene method (A), a classical method (B) and a MW-assisted-s.f.c. method (C) at different times.

Sample name	HCl silica treatment	Procedure	Solvent	Temperature (°C)	Time (min)	TOC (mmolC/gr of silica)	SD
CS01	25%	MW	dry toluene	150	5	0,89	0,10
CS02	25%	MW	dry toluene	150	10	1,03	0,24
CS03	25%	MW	dry toluene	150	15	0,93	0,25
CS04	25%	MW	dry toluene	150	30	1,01	0,16
CS05	25%	reflux	dry toluene	150	180	0,70	0,19
CS06	25%	MW	dry toluene	110	10	1,21	0,08
CS07	25%	MW	dry toluene	130	10	1,52	0,14
CS08	25%	MW	dry toluene	150	10	2,19	0,24
CS09	25%	MW	dry toluene	170	10	2,53	0,07
CS10	25%	MW	-	130	10	2,19	0,01
CS11	25%	MW	-	150	10	2,38	0,14
CS12	25%	MW	-	170	10	2,79	0,10
CS13	25%	MW	dry toluene	130	10	0,69	0,13
CS14	25%	MW	dry toluene	130	10	0,81	0,03
CS15	25%	Sailed oil bath	dry toluene	130	10	0,58	0,07
CS16	25%	Sailed oil bath	dry toluene	130	10	0,71	0,05
CS17	25%	Sailed oil bath	dry toluene	130	10	0,54	0,02
CS18	25%	MW	dry toluene	130	10	0,85	0,10
CS19	25%	MW	dry toluene	130	10	1,25	0,13
CS20	25%	MW	dry toluene	130	10	1,94	0,18
CS21	25%	MW	dry toluene	130	10	1,13	0,36
CS22	25%	MW	dry toluene	130	10	1,40	0,46
CS23	25%	MW	dry toluene	130	10	1,73	0,12
CS24	25%	MW	dry toluene	130	10	1,94	0,05
CS25	25%	MW	dry toluene	130	10	2,04	0,14
CS26	25%	MW	dry toluene	130	10	2,08	0,10
CS27	25%	MW	dry toluene	130	10	2,03	0,15
CS28	25%	MW	dry toluene	130	10	2,24	0,03
CS29	25%	MW	dry toluene	130	10	2,11	0,14
CS30	25%	MW	dry toluene	130	10	2,07	0,04
CS31	25%	reflux	dry toluene	130	10	2,34	0,01
CS32	5%	MW	dry toluene	150	15	2,46	0,01
CS33	15%	MW	dry toluene	150	15	2,09	0,02
CS34	25%	MW	dry toluene	150	15	1,92	0,04
CS35	5%	MW	dry toluene	165	15	2,26	0,02
CS36	15%	MW	dry toluene	165	15	1,10	0,01
CS37	25%	MW	dry toluene	165	15	2,05	0,01
CS38	5%	MW	dry toluene	130	10	1,44	0,01
CS39	15%	MW	dry toluene	130	10	1,60	0,01
CS40	25%	MW	dry toluene	130	10	1,72	0,02

CS41	5%	MW	dry toluene	110	10	0,93	0,02
CS42	15%	MW	dry toluene	110	10	1,17	0,00
CS43	25%	MW	dry toluene	110	10	0,81	0,01
CS44	5%	reflux	dry toluene	150	240	1,74	0,31
CS45	15%	reflux	dry toluene	150	240	2,49	0,01
CS46	25%	reflux	dry toluene	150	240	0,90	0,03
CS47	5%	reflux	dry toluene	150	over night	2,16	0,01
CS48	15%	reflux	dry toluene	150	over night	2,76	0,03
CS49	25%	reflux	dry toluene	150	over night	2,15	0,02
CS50	25%	MW	-	130°C	10	1,55	0,07
CS51	25%	MW	-	130°C	10	2,95	0,03
CS52	25%	MW	-	130°C	10	2,30	0,05
CS53	25%	MW	-	130°C	10	2,92	0,08

Validation set table

Table 2. TOC values (mmol C/gr of catalyst) of mesoporous silica samples, used for validation, functionalized by a MW-assisted-Toluene method (A), a classical method (B) and a MW-assisted-s.f.c. method (C) at different times.

Sample name	HCl silica treatment	Procedure	Solvent	Temperature (°C)	Time (min)	TOC (mmolC/gr of silica)	SD
VS01	25%	MW	dry toluene	150	15	0,93	0,25
VS02	25%	reflux	dry toluene	150	180	0,70	0,19
VS03	25%	reflux	dry toluene	150	360	1,03	0,14
VS04	25%	MW	-	110	10	1,97	0,16
VS05	25%	MW	dry toluene	130	10	1,25	0,13
VS06	25%	MW	dry toluene	130	10	2,01	0,16
VS07	25%	MW	dry toluene	130	10	1,94	0,05
VS08	25%	MW	dry toluene	130	10	2,24	0,03
VS09	25%	MW	dry toluene	130	10	2,05	0,17
VS10	25%	MW	dry toluene	130	10	2,13	0,20
VS11	25%	MW	dry toluene	130	10	2,33	0,02
VS12	5%	MW	dry toluene	110	10	0,93	0,02
VS13	25%	MW	dry toluene	110	10	0,81	0,01
VS14	15%	reflux	dry toluene	150	240	2,49	0,01
VS15	25%	MW	-	130°C	10	1,43	0,18