Supporting Information

Hybrid Sulfonic Acid Catalysts based on Silica -Supported Poly(styrene sulfonic acid) Brush Materials and their Application in Ester Hydrolysis

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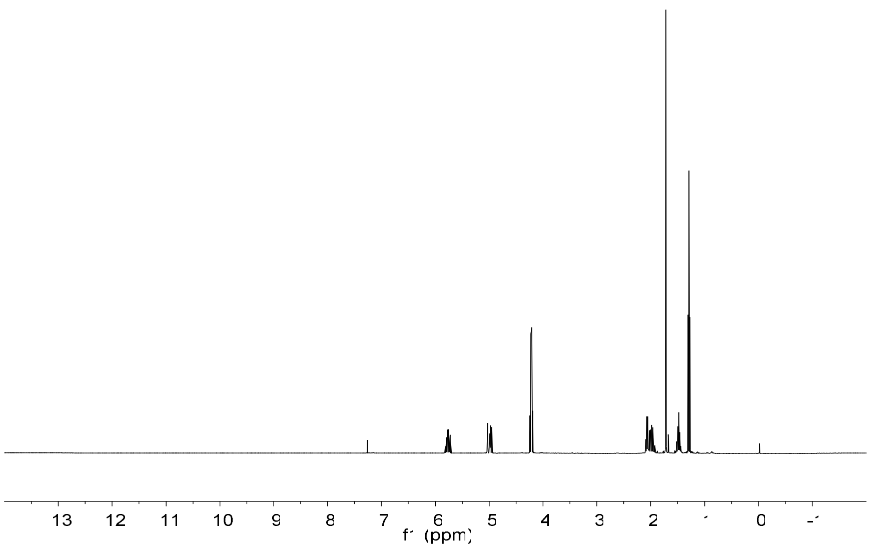

Figure S1. [1]H NMR of ethyl 2-chloro-2-methyl-6-heptenoate

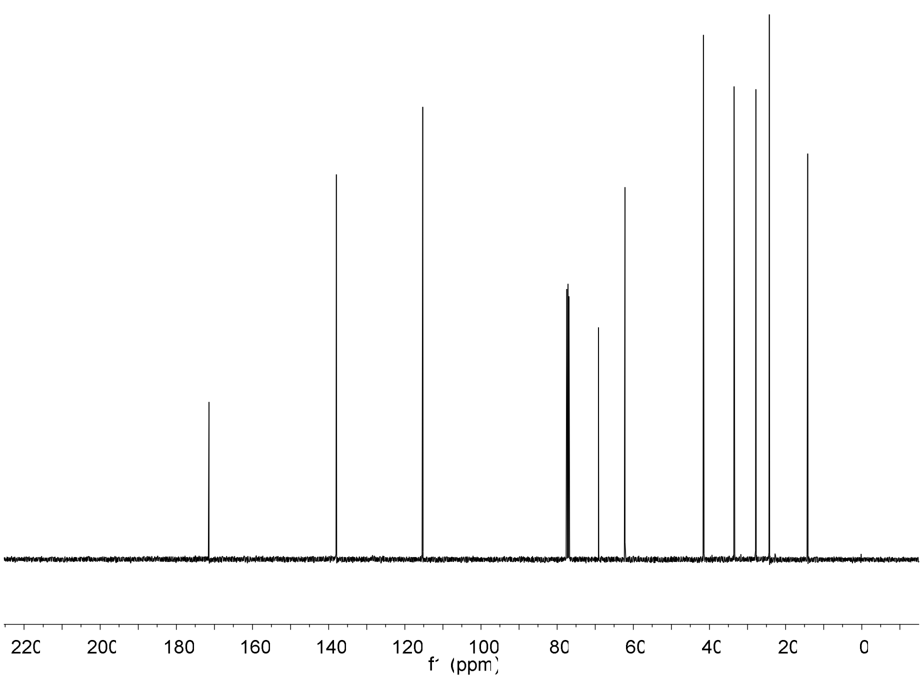

Figure S2.[13]C NMR of ethyl 2-chloro-2-methyl-6-heptenoate

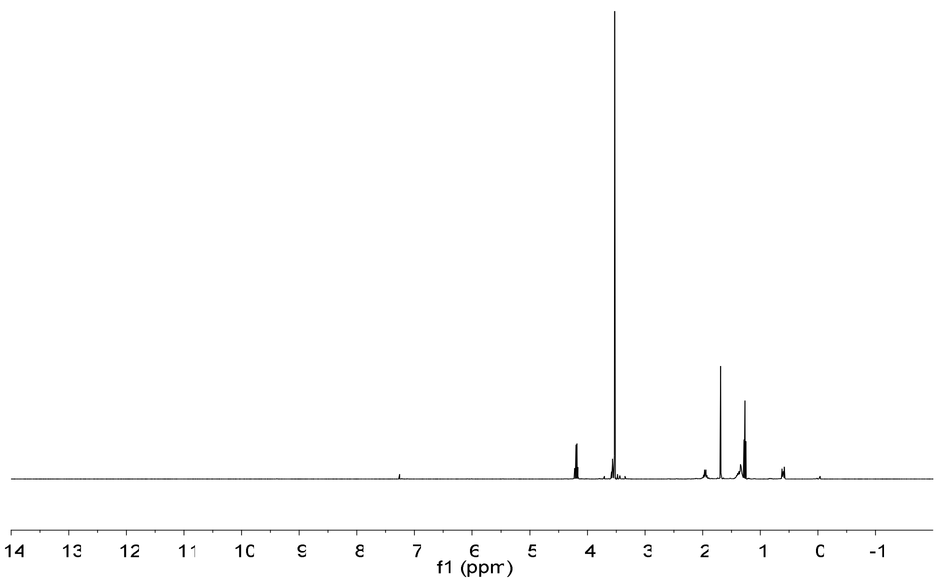

Figure S3. [1]H of ethyl 2-chloro-2-methyl-7-(trimethoxysilyl) heptanoate

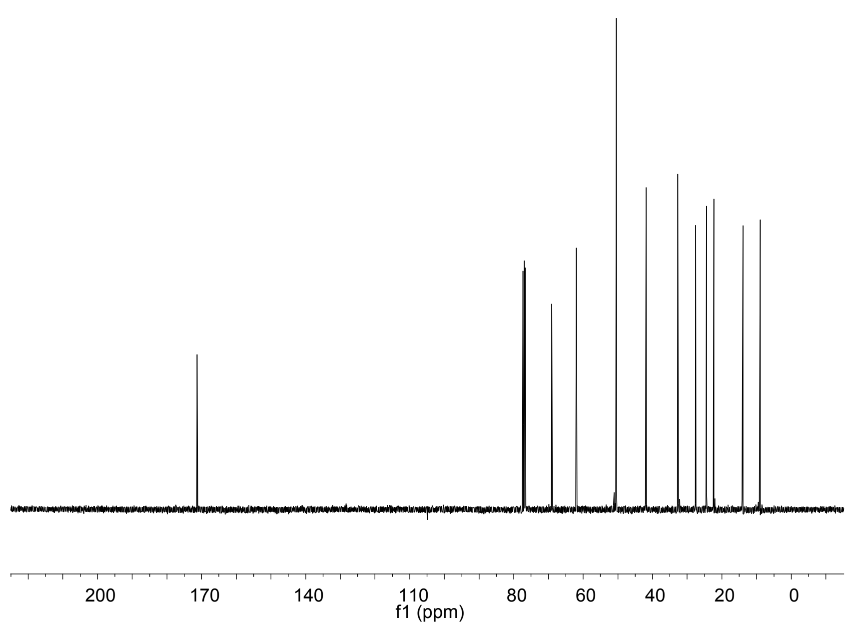

Figure S4. [13]C of ethyl 2-chloro-2-methyl-7-(trimethoxysilyl) heptanoate

Calculation of number of initiators on the silica surface:

Initiator density = initiator loading × N_A/SA

Initiator loading = mmol of initiator / g of sample

Initiator density = no. of initiator / nm^2 of surface

Surface area (SA) of Cab-O-Sil M5 = 200 m^2/g

Table S1.Polymer loadings of SiO_2@PSt.

Materials	Polymer loading (from TGA)	Polymer loading (calculated from mass balance)
SiO_2@alkyl-PS	0.55	0.64
SiO_2@ester-PS	0.41	0.44

Calculation of polymer loading (from TGA):

W_i= w.t.% of initiator / w.t.% of silica (in the SiO_2@initiator)

W_o = w.t. % of organic groups / w.t. % of silica (in the SiO_2@PS)

W_p = w.t. % of polymer / w.t. % of silica = W_o - W_i

Polymer loading (w.t. %) = $W_p / (1+W_p+W_i)$

Calculation of polymer loading (from mass balance):

Polymer loading (w.t. %)

= (the mass of styrene × conv.) / (the mass of silica supported initiator + the mass of styrene × conv.)

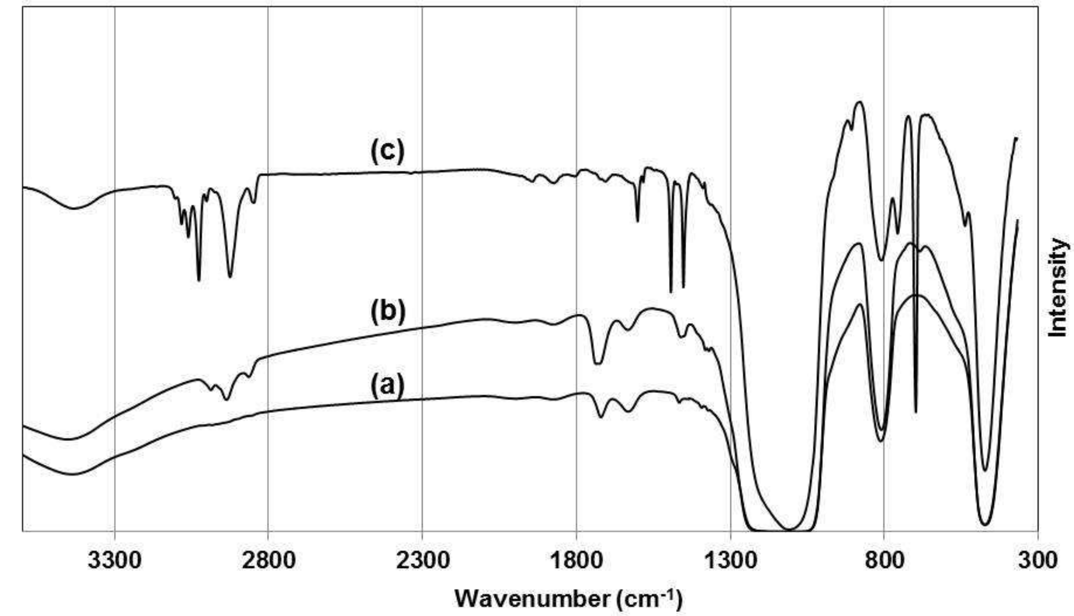

Figure S5. FT-IR of SiO_2@ester initiator (a); SiO_2@alkyl initiator (b); SiO_2@ester-PSt (c).

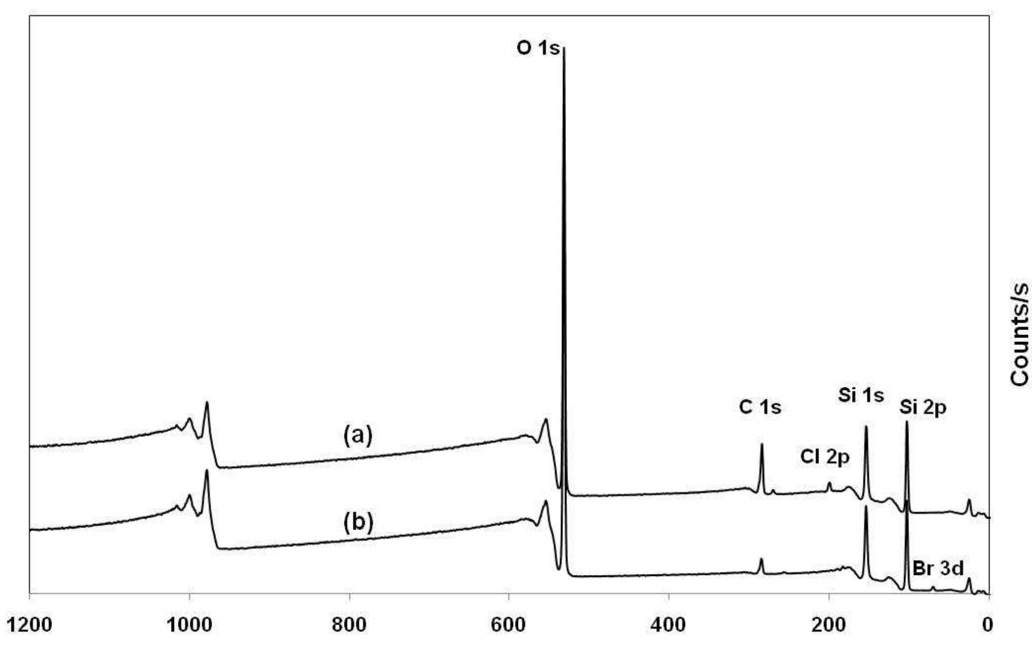

Figure S6. XPS spectra of SiO_2@alkyl initiator (a); SiO_2@ester initiator (b).

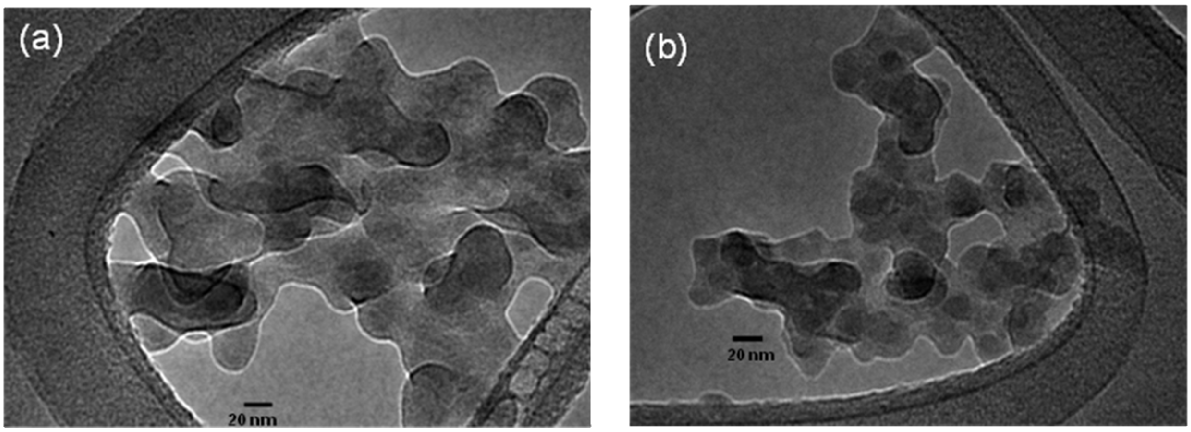

Figure S7. TEM images of SiO_2@alkyl-PS (a); SiO_2@ester-PS (b), at identical magnification.

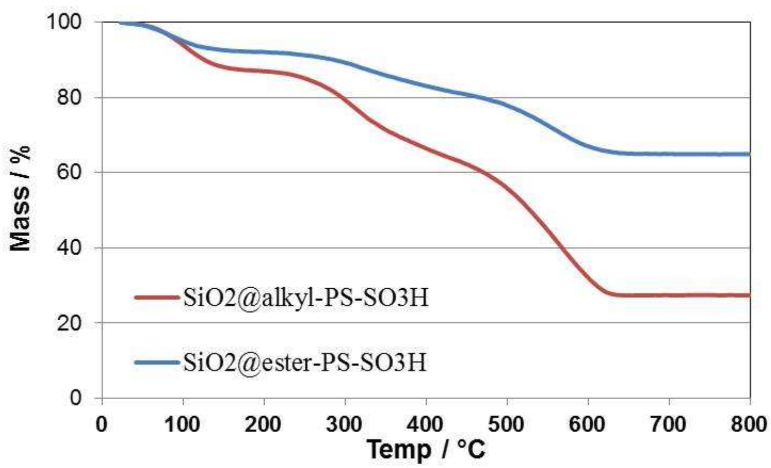

Figure S8. TGA of SiO_2@alkyl-PS-SO_3H.

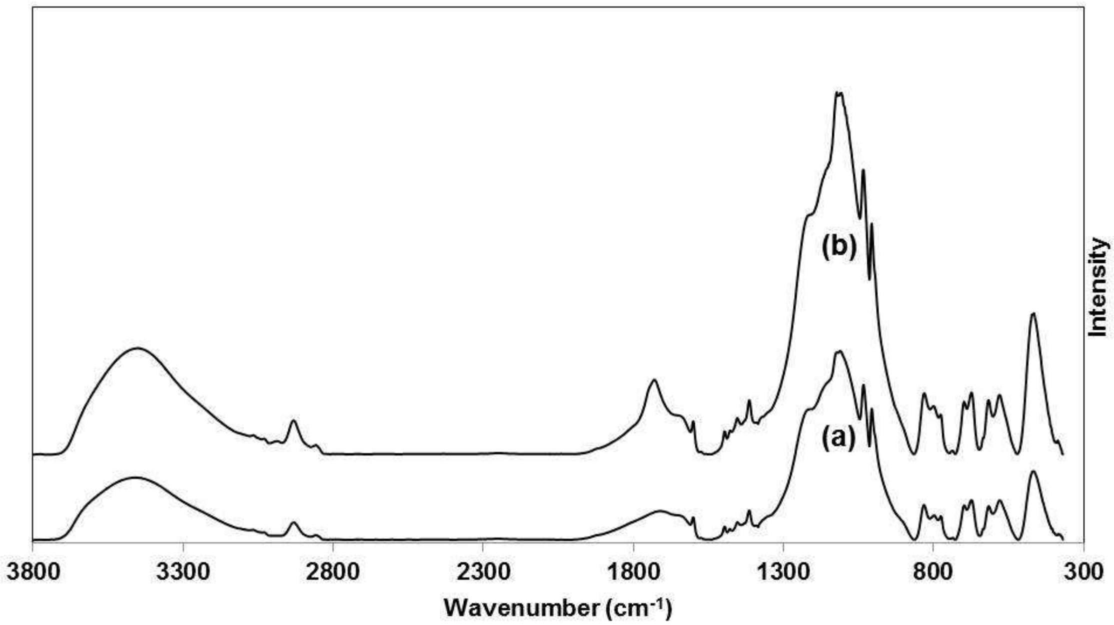

Figure S9.FT-IR spectra of SiO_2@alkyl-PS-SO_3H (a); SiO_2@alkyl-PS-SO_3H after run 1 (b).

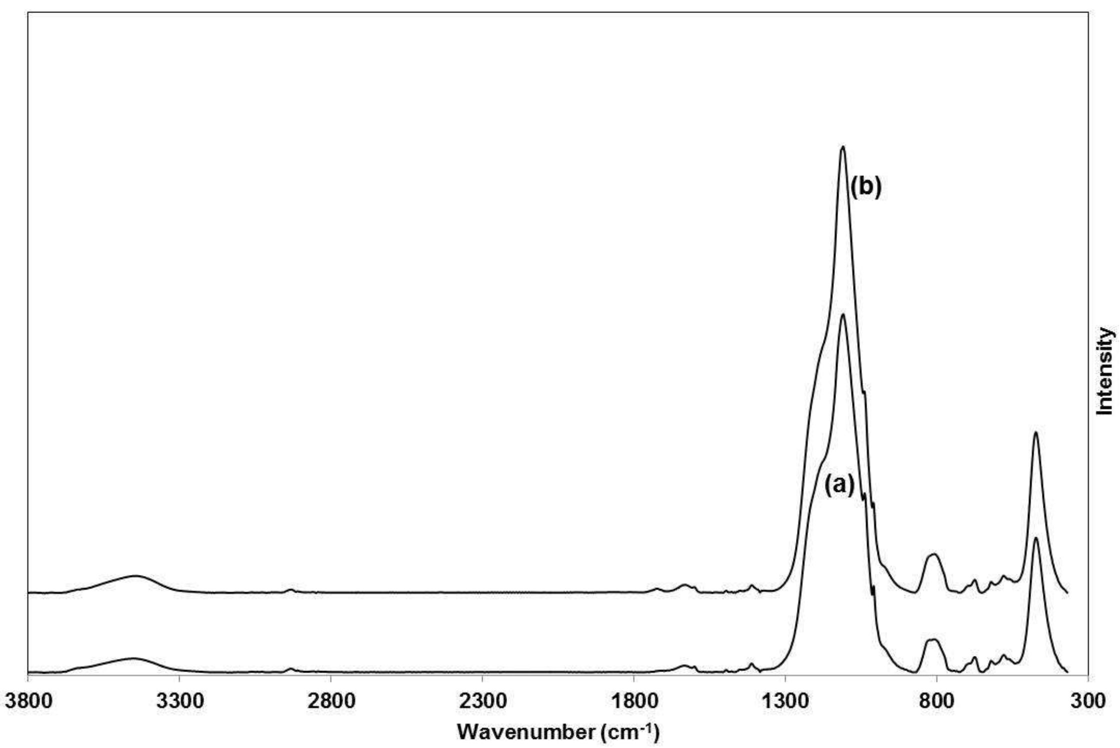

Figure S10.FT-IR spectra of SiO_2@ester-PS-SO_3H (a); SiO_2@ester-PS-SO_3H after run 1 (b).

Table S2. EA of the fresh SiO_2@alkyl-PS-SO_3H and the recycled ones.

Catalysts	C wt%	S wt%	Si wt%	S/C	C mmol/g SiO_2
Fresh	33.15	10.45	13.5	0.118	95.6
After 1st run	30.71	7.4	15.12	0.090	79.0
After 3rd run	32.83	7.5	20.01	0.086	63.9

Table S3. EA of the fresh SiO_2@ester-PS-SO_3H and the recycled ones.

Catalysts	C wt%	S wt%	Si wt%	S/C	C mmol/g SiO_2
Fresh	15.64	4.85	32.19	0.116	18.9
After 1st run	12.60	3.72	45.74	0.110	10.7
After 3rd run	8.45	1.395	48.72	0.062	6.75

Table S4. Surface initiated ATRP on SiO_2@ester initiator _2.

Materials	Loading of SiO2@ester initiator_2 (mmol/g)	[M]/[SiO_2 @initiator]	Conv.	$[M]_{polymerized}$/ [SiO_2@initiator]	Organic loading	Organic loading after re-washing
SiO_2@ester -PS-2	0.44	50	71%	35.5	61.5%	61.3%

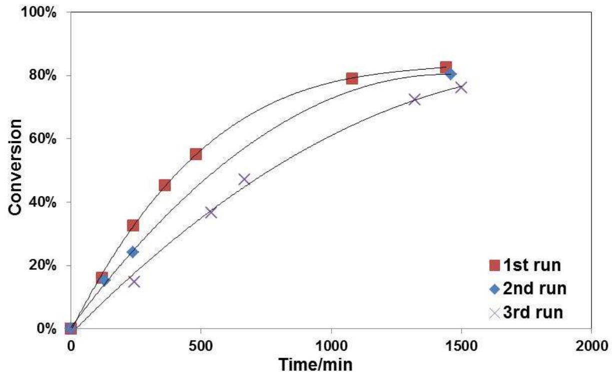

Figure S11. Kinetics of SiO_2@ester-PS-SO_3H_2 during recycles. (1.25 mol% catalyst loading, 60 °C)

Table S5. EA of the fresh SiO_2@ester-PS-SO_3H_2 and the recycled catalysts.

Catalysts	C wt%	S wt%	Si wt%	S/C	C mmol/g SiO_2
Fresh	26.43	7.09	15.12	0.100	68.0
After 1st run	28.05	6.70	20.03	0.089	54.5
After 2nd run	23.87	-	21.83	-	42.6