

Supporting information

**Sulfated Zirconia an Efficient Catalyst for the
Friedel-Crafts Mono alkylation of Resorcinol with
Methyl tertiary butyl ether to 4-Tertiary
butylresorcinol**

Vijaykumar S Marakatti,^a Shivanna Marappa,^b Eric M Gaigneaux^{a*}

^aInstitute of Condensed Matter and Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Université catholique de Louvain (UCLouvain), Place Louis Pasteur 1, L4.01.09, B-1348 Louvain-la-Neuve, Belgium.

^bJawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur, Bangalore, 560064, India.

**corresponding author: eric.gaigneaux@uclouvain.be*

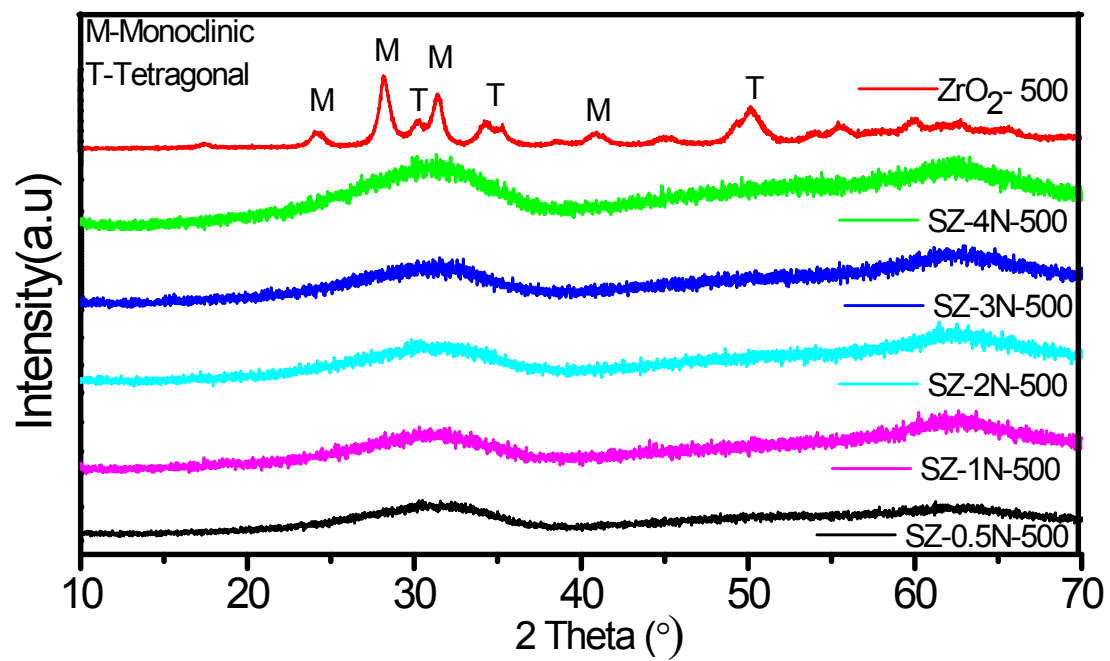


Figure S1. XRD patterns of ZrO₂ and sulfated zirconia catalysts calcined at 500 °C.

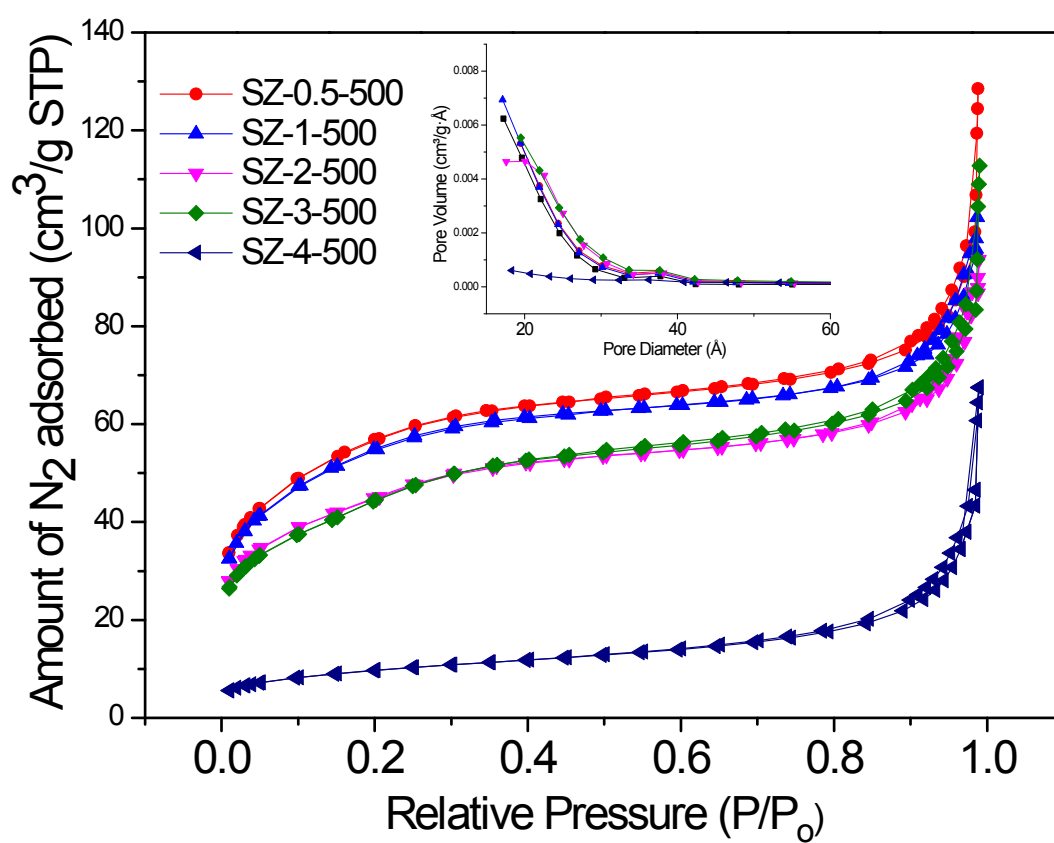


Figure S2. Nitrogen adsorption–desorption isotherms and pore size distribution of SZ catalysts calcined at 500 °C.

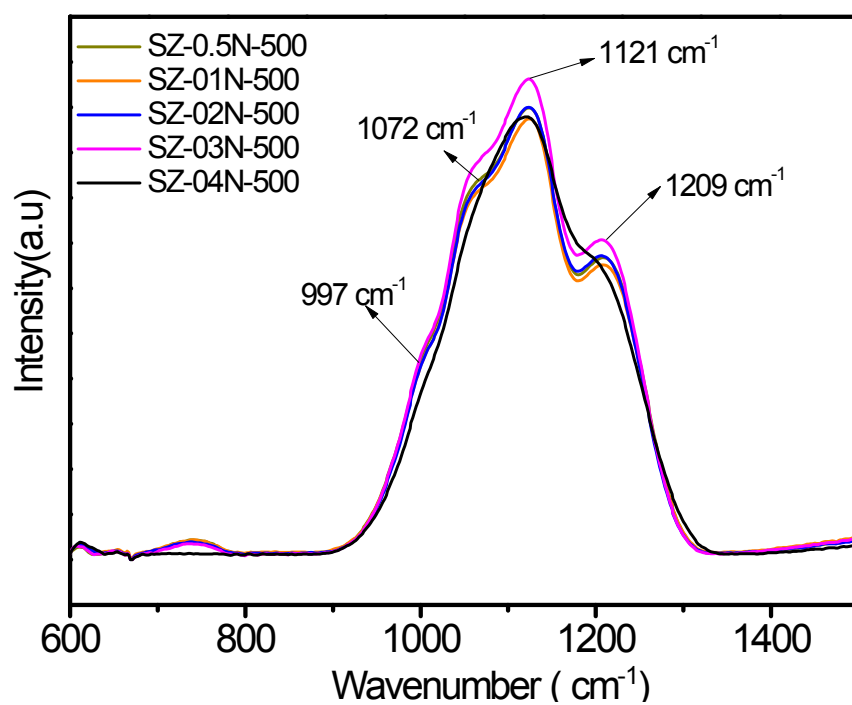


Figure S3. FT-IR spectra of sulfated zirconia catalysts calcined at 500 °C

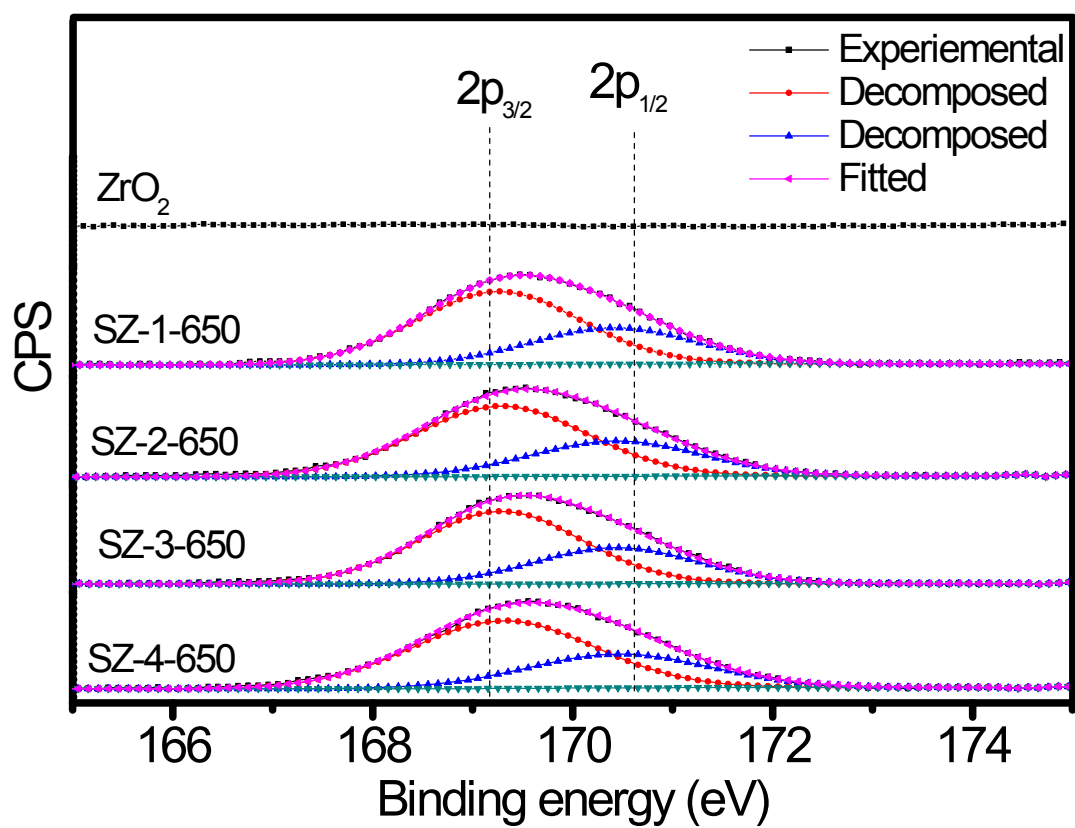


Figure S4. Sulfur 2p_{3/2} ad 2p_{1/2} XPS spectra of SZ-650 catalysts.

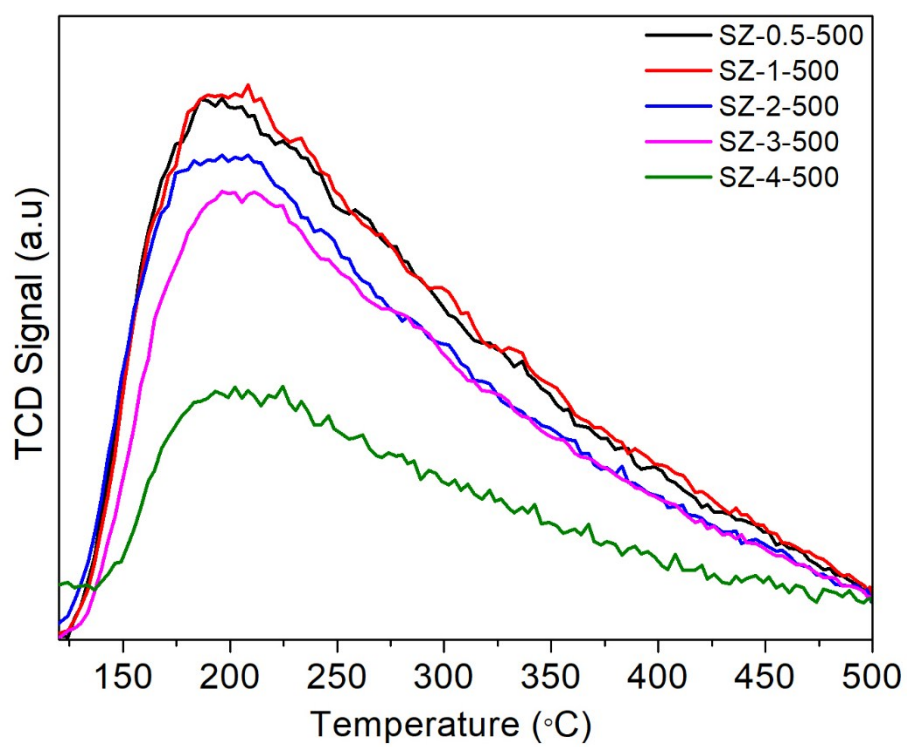


Figure S5. TPD-NH₃ profiles of sulfated zirconia catalysts calcined at 500 °C.

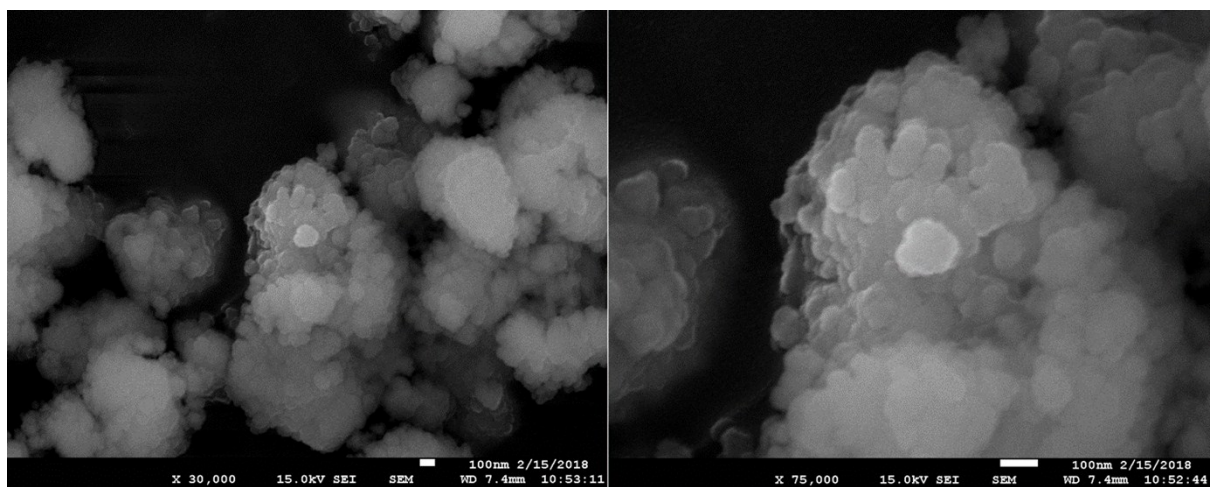


Figure S6. SEM image of SZ-1-650 catalyst.

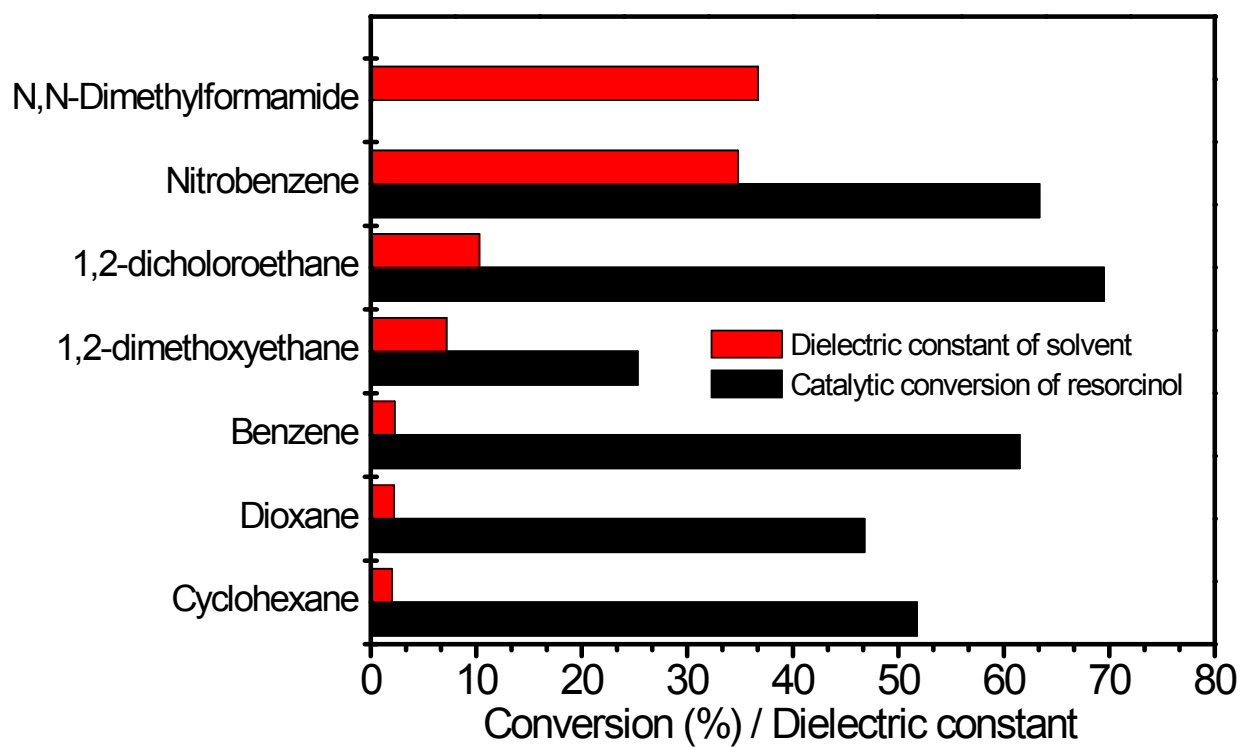


Figure S7. Role of dielectric constant on catalytic conversion of resorcinol.

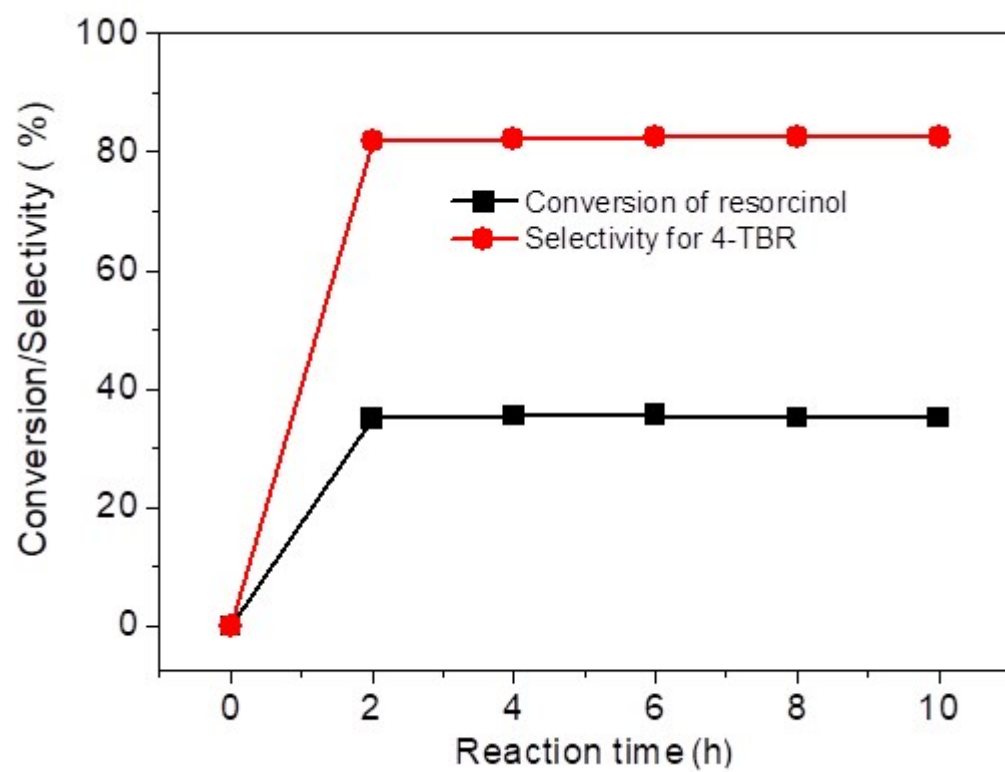


Figure. S8 Leaching test of SZ catalyst in resorcinol alkylation reaction.

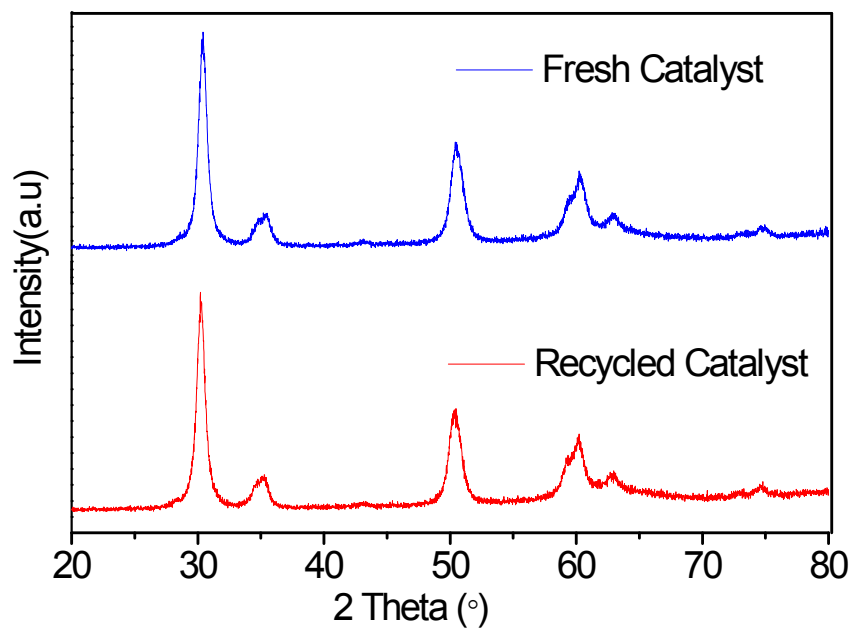


Figure S9. The XRD pattern of the fresh and recycled catalysts.

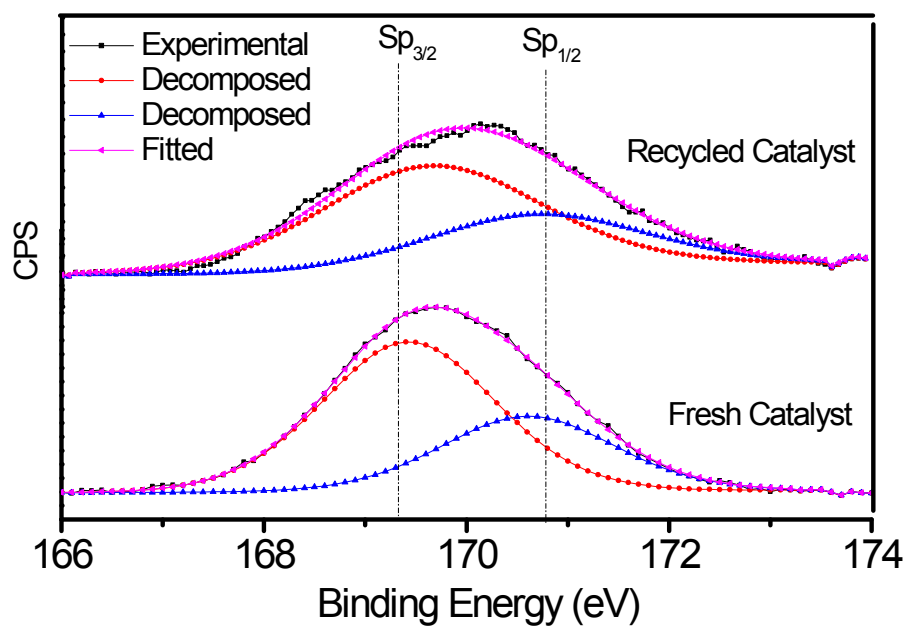


Figure S10. Sulfur $2p_{3/2}$ and $2p_{1/2}$ XPS spectra of SZ-650 catalysts after recycle.

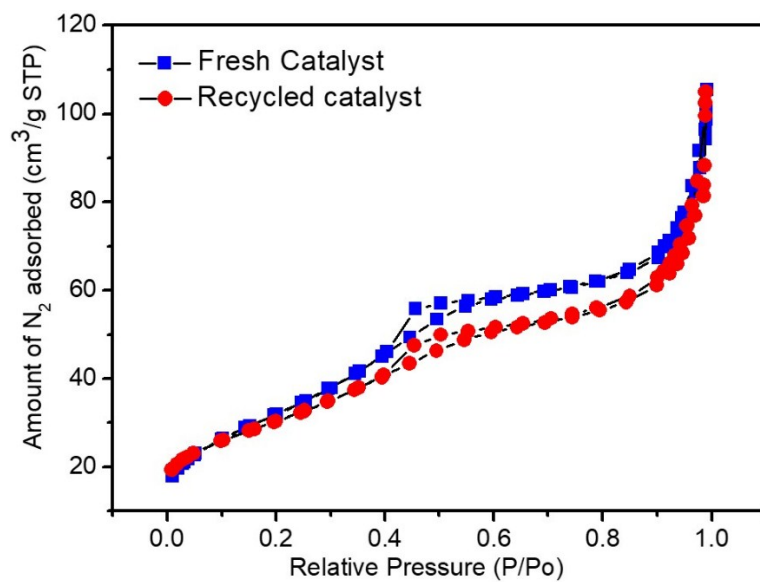


Figure S11. N₂ sorption isotherm of fresh and final recycled SZ-1N-650 catalyst.

Table S1. Correlation of initial catalytic activity (2 h) with the acidity of the SZ catalysts.

Catalyst	Conversion of resorcinol (mol %)	Selectivity (%)				
		R-MTBE	2-TBR	4-TBR	4,6- DTBR	Others
SZ-0.5-500	34	3	5	82	9	1.0
SZ-1-500	43	2	3	82	11	1.0
SZ-2-500	39	17	6	72	4	0.8
SZ-3-500	22	16	6	72	4	1.3
SZ-4-500	14	20	6	70	2	1.4
SZ-0.5-650	41	2	1	85	11	0.8
SZ-1-650	35	2	5	82	10	0.7
SZ-2-650	33	2	5	81	10	1.3
SZ-3-650	31	3	5	82	9	1.0
SZ-4-650	26	5	7	80	6	1.2

Reaction Conditions: catalyst amount = 0.22 g, temperature = 60 °C; resorcinol= 2.2 g, MTBE=7.2 ml, time= 2 h.

Table S2. The Brönsted and Lewis acidity measurement of sulfated zirconia catalyst determined by Py-FTIR study and their catalytic activity.

Catalysts	BrÖnsted Acidity(B) (-%)	Lewis Acidity(L) (%)	B/L	Conversion of resorcinol (mol %)	Selectivity for 4-TBR
SZ-0.5-650	29	71	0.41	41	85
SZ-1-650	36	64	0.57	35	82
SZ-2-650	42	58	0.73	33	81
SZ-3-650	40	59	0.68	30	82
SZ-4-650	34	65	0.52	26	80

Reaction Conditions: catalyst amount = 0.22 g, temperature = 60 °C; resorcinol= 2.2 g, MTBE=7.2 ml, time= 2 h.

Table S3. Catalytic activity over different alkylating agent.

Alkylating agent	Conversion of resorcinol (mol %)	Selectivity (%)				
		R-MTBE	2- TBR	4-TBR	4,6- DTBR	Others
MTBE	69	0.4	0.3	72	26	0.5
TBA	37	14	7	73	5	1.5
DTBDC	70	--	--	67	32	--

Reaction Conditions: Catalyst =SZ-1N, catalyst amount = 0.22 g, temperature = 60 °C; resorcinol= 2.2 gram, MTBE=4.8 ml, TBA= 4 ml, DTBDC= 2.1 g, 1, 2-dichloroethane = 2 ml.