

CAPONE

Carbenes in Porous Networks

CP2D-EFC 2009

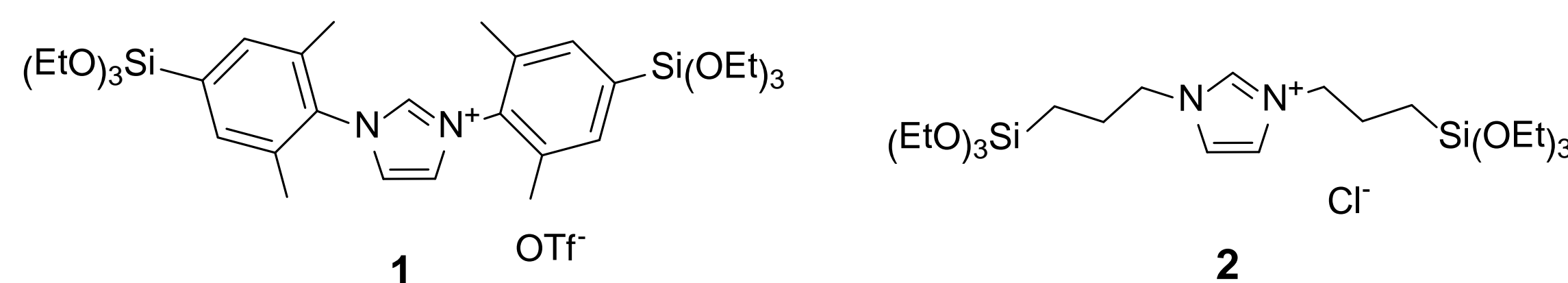
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1. Introduction

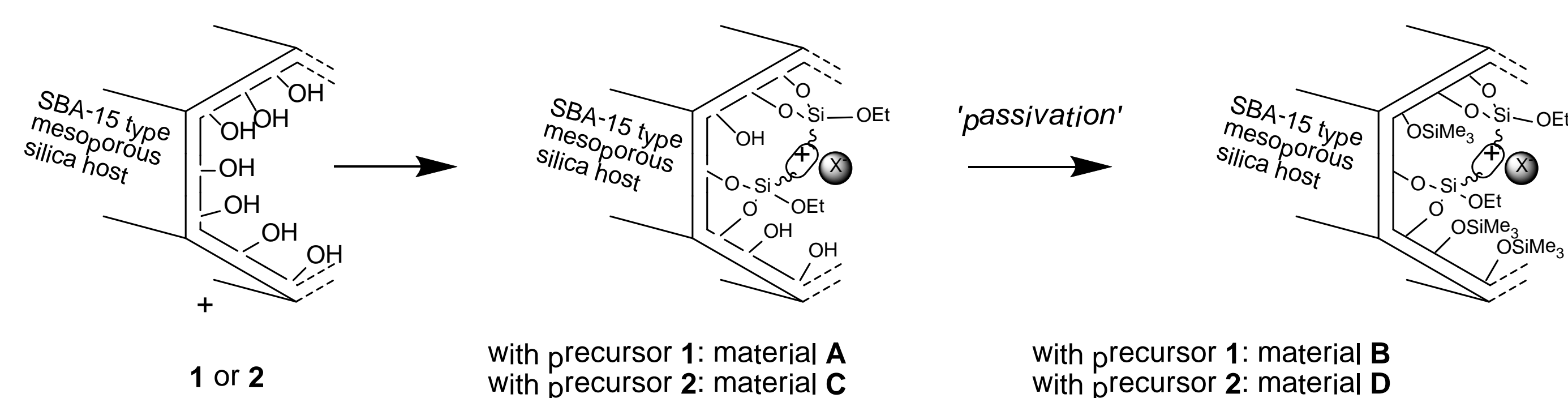
We focused on the synthesis of mesoporous SBA-15 type silica bearing ionic imidazolium substructures. The synthesis of the functional materials was achieved both *via* post-synthesis grafting reactions using *bis*-silylated imidazolium precursors onto a mesoporous SBA-15 type silica support and 'one-pot' hydrolysis-polycondensation reactions. The obtained materials were used as heterogeneous organocatalysts in Henry reactions and the cycloaddition of CO₂ to epoxides.

2. Synthesis and characterization of the materials

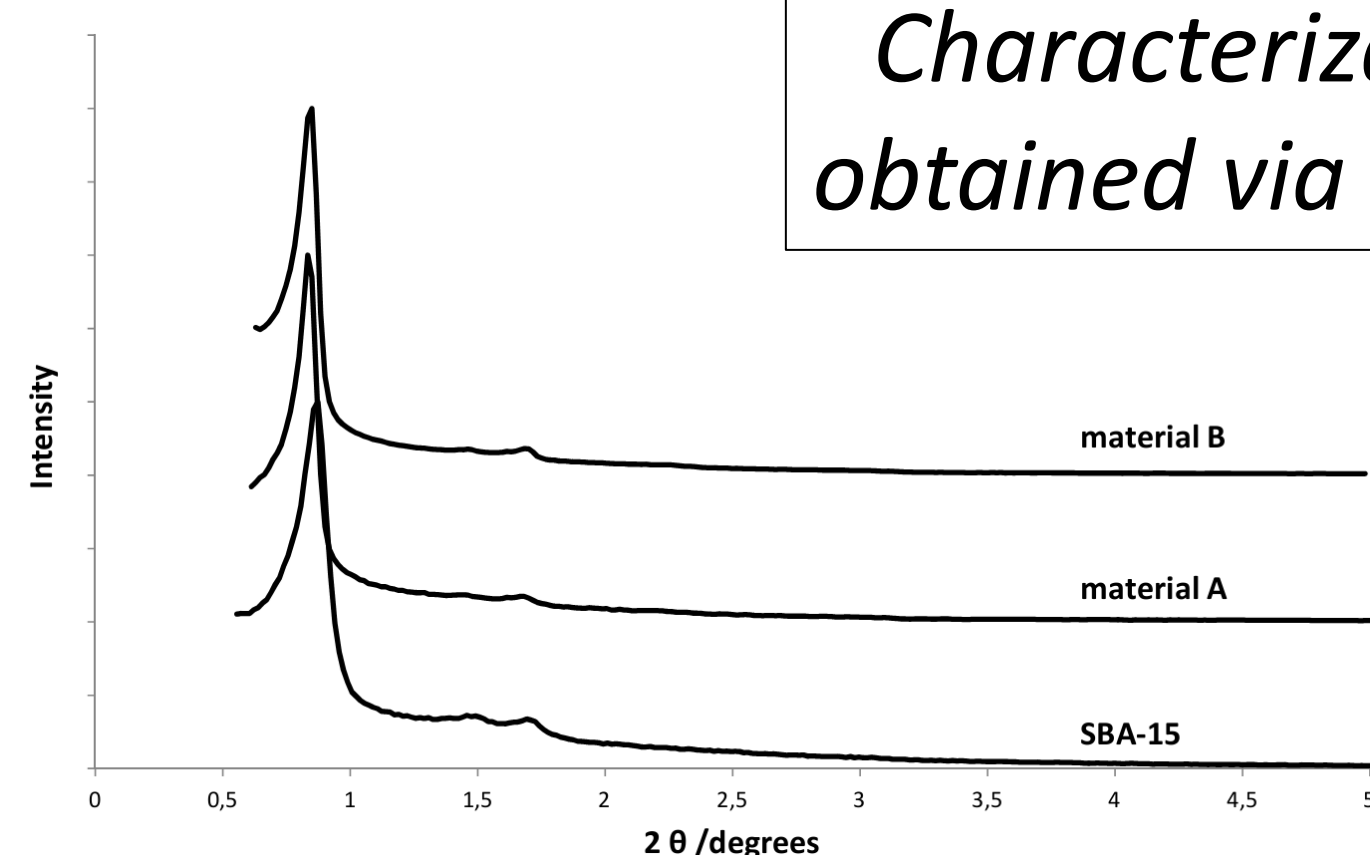
Used ionic precursors



Post synthesis grafting and passivation reactions

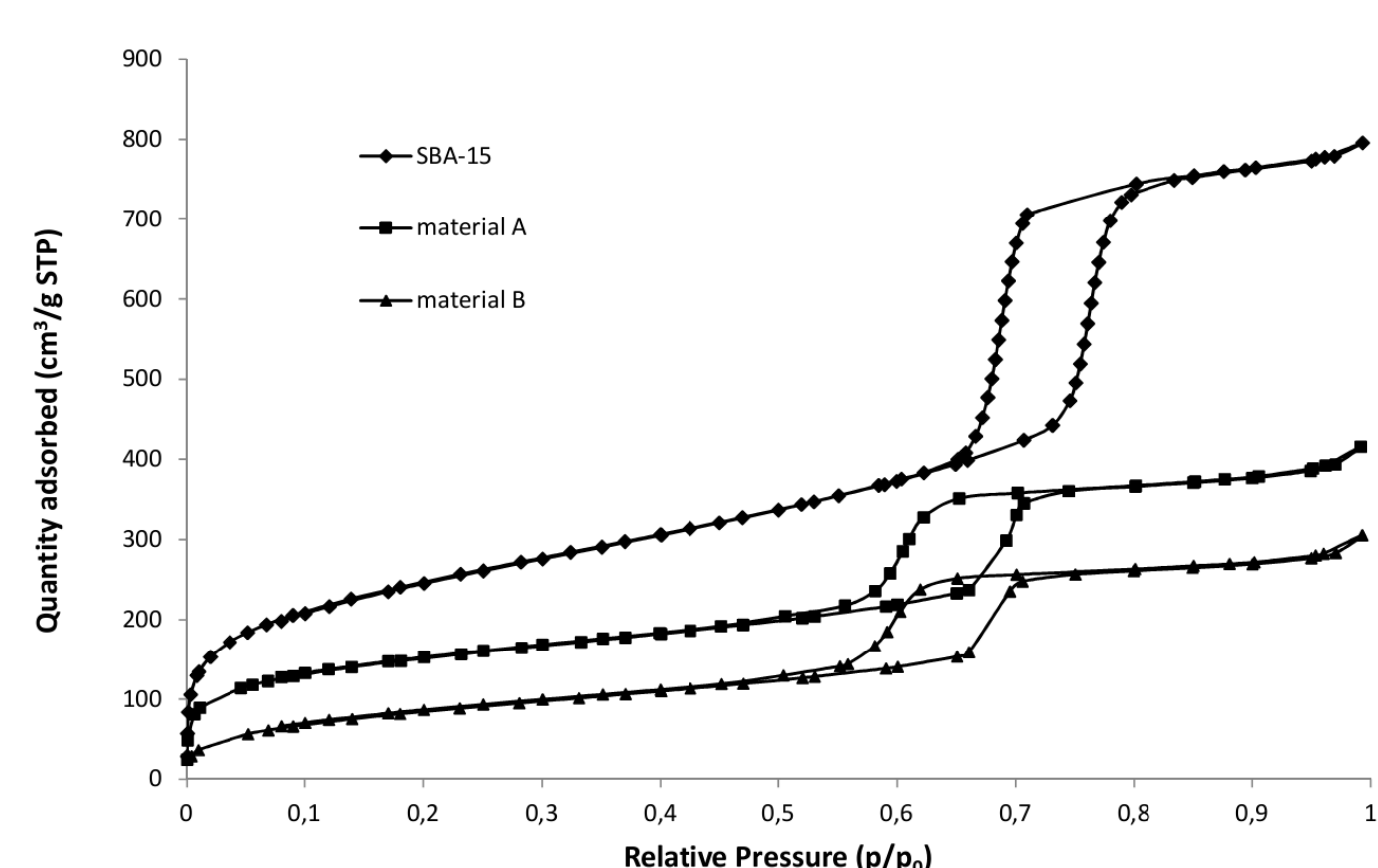


Characterization of the materials obtained via post-synthesis grafting

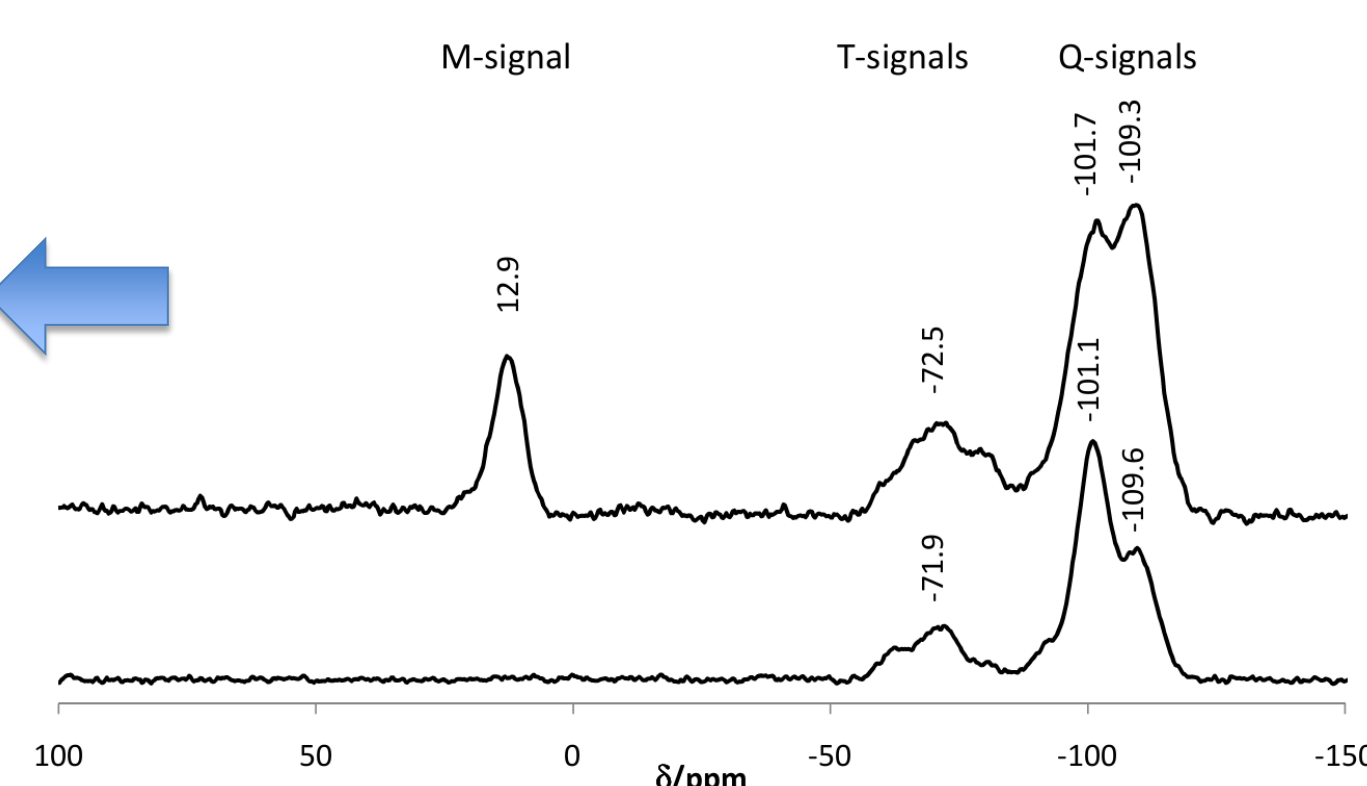


X-ray diffraction: preservation of the regular architectures on a mesoscopic length scale

¹³C CP-MAS solid state NMR spectroscopy: determination of the amount of grafted ionic species

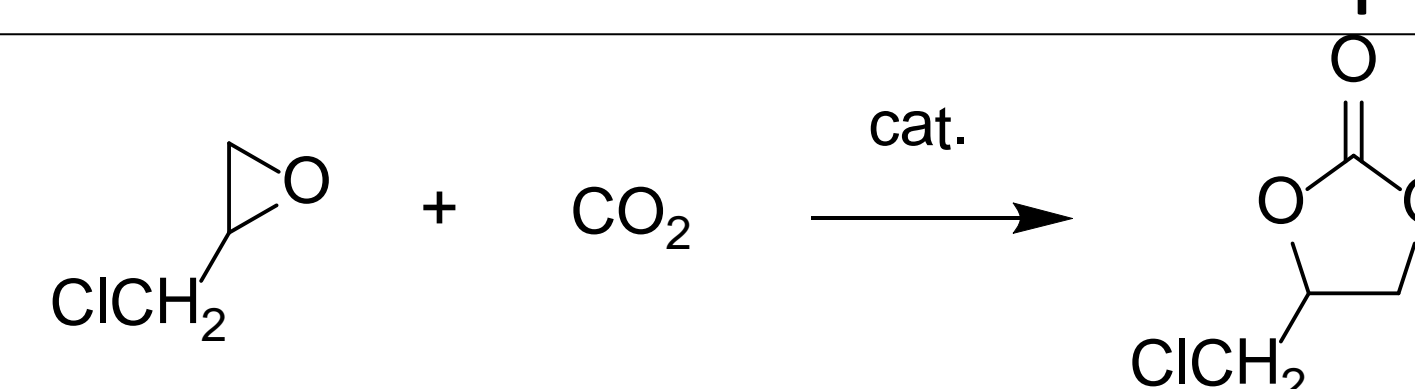


Nitrogen sorption experiments: determination of the surface properties of the materials



3. Applications in Organocatalysis

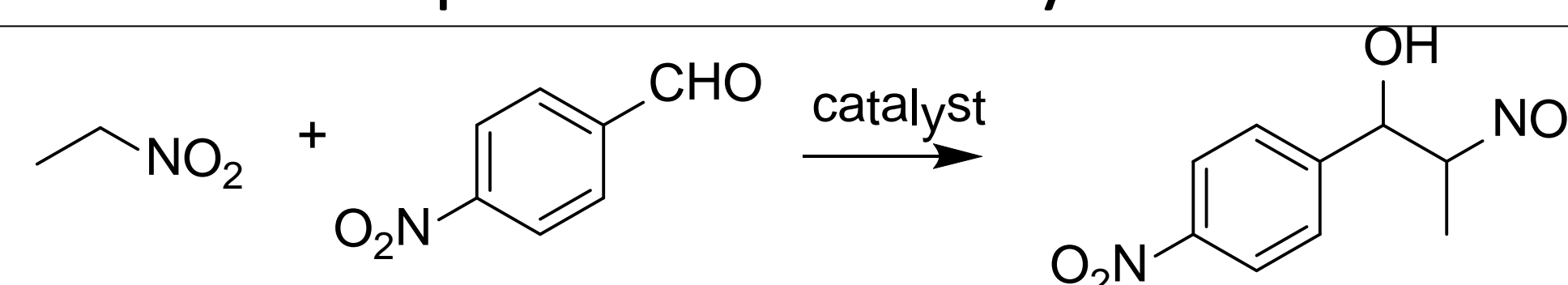
Cycloaddition of carbon dioxide to epoxides



Entry	Catalyst ^a	Conversion (%) ^b	Selectivity (%) ^c	Entry	Catalyst ^a	Conversion (%) ^b	Selectivity (%) ^c
1	SBA-15, 100mg ^b	13.2	100	10	material C, 100 mg 1 st cycle	100	94.4
2	material A, 103 mg 1 st cycle	97.3	92.4	11	material C, 95 mg 2 nd cycle	100	94.0
3	material A, 95 mg 2 nd cycle	81.9	94.4	12	material C, 80 mg 3 rd cycle	100	95.3
4	material A, 65 mg 3 rd cycle	76.4	94.1	13	material C, 54 mg 4 th cycle	98.3	95.4
5	material A, 63 mg 4 th cycle	65.4	95.8	14	material D, 102 mg 1 st cycle	100	94.4
6	material B, 97 mg 1 st cycle	100	93.0	15	material D, 88 mg 2 nd cycle	100	94.2
7	material B, 91 mg 2 nd cycle	90.5	94.1	16	material D, 75 mg 3 rd cycle	100	95.0
8	material B, 64 mg 3 rd cycle	81.6	94.1	17	material D, 61 mg 4 th cycle	77.8	77.1
9	material B, 47 mg 4 th cycle	68.1	94.2				

^a Conditions of the reaction: 18 mmol of epichlorohydrin, 6.9 bar of CO₂, 130°C, 4 h; ^b Specific surface area S_{BET}: 856m²/g; total pore volume: 0.98 cm³/g, average pore diameter: 7 nm; ^c Conversion and selectivity determined by GC

Henry reaction of p-nitrobenzaldehyde with nitroethane



Entry	Aldehyde	Catalyst	reaction time/h	reaction temperature /°C	Conversion ^b %	syn/anti ratio ^b	Entry	Aldehyde	Catalyst	reaction time/h	reaction temperature /°C	Conversion ^b %	syn/anti ratio ^b
1	p-nitro-benzaldehyde	none	4	RT	0	-	13	p-nitro-benzaldehyde	material C, 15%	4	RT	13	49:51
2	p-nitro-benzaldehyde	parent SBA-15	24	RT	0	-	14	p-nitro-benzaldehyde	material D, 15%	4	RT	85	54:46
3	p-nitro-benzaldehyde	passivated SBA-15	24	RT	12	46:54	15	p-nitro-benzaldehyde	material B, 15%	72	RT	87	58:42
4	p-nitro-benzaldehyde	BMIM-PF ₆	24	90	18	46:54	16	p-nitro-benzaldehyde	material B, 15%	72	RT	5	57:43
5	p-nitro-benzaldehyde	material A, 15%	72	RT	53	48:52	17	p-nitro-benzaldehyde	material B, 15%	24	RT	87	59:41
6	p-nitro-benzaldehyde	material A, 15%	72	45	<1	-	18	p-nitro-benzaldehyde	material B, 15%	48	40	45	70:30
7	p-nitro-benzaldehyde	material A, 15%	4	RT	21	57:43	19	p-nitro-benzaldehyde	material E, 15%	4	RT	96	58:42
8	p-nitro-benzaldehyde	material B, 15% 1st cycle	4	RT	99	58:42	20	p-nitro-benzaldehyde	material F, 15%	4	RT	75	58:42
9	p-nitro-benzaldehyde	material B, 15% 2nd cycle	4	RT	99	58:42	21	p-nitro-benzaldehyde	material G, 15%	24	RT	7	53:47
10	p-nitro-benzaldehyde	material B, 15% 3rd cycle	4	RT	98	58:42	22	p-nitro-benzaldehyde	material H, 15%	24	RT	<1	-
11	p-nitro-benzaldehyde	material B, 15% 4th cycle	4	RT	98	58:42	23	p-nitro-benzaldehyde	material I, 15%	4	RT	20	55:45
12	p-nitro-benzaldehyde	material B, 15% 5th cycle	4	RT	96	58:42							

^a Reaction conditions: 1 eq. aldehyde, 20 eq. nitroethane, 0.15 eq. catalyst (calculated in base of the imidazolium derived loading for materials A-F or equivalent mass of solid for SBA-15 and passivated SBA-15). ^b Conversion and selectivity determined by NMR.

4. Conclusion

Our results show that the catalytic activities of SBA-15 type mesoporous silicas containing covalently tethered imidazolium groups depend on various parameters such as the nature of the grafted cationic species, the nature of the counter ion, the hydrophobicity of the surface and the condensation degree of the silica support. Furthermore, synergetic effects between two or more of these aspects may further modify the catalytic properties of the materials. For this reason, our results indicate that the materials reported here cannot simply be considered as simple silica supported imidazolium salts. The detailed comprehension of all interactions between reactants, substrates, support and catalyst should enable us to design more efficient heterogeneous organocatalysts in the near future.

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