ε-Caprolactone polymerization using titanium complexes immobilized onto silica based materials functionalized with ionic liquids: Insights into steric, electronic and support effects

Electronic Supplementary Information

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1. Preparation of ionic liquids

1.1. Preparation of 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (IMILCl)

The ionic liquid 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (IMILCl) was synthesized according to the procedure reported in the literature.[1] In the experiment, 1-methyl-imidazol (2.2 mL, 28 mmol) and (3-chloropropyl) triethoxysilane (6.7 mL, 28 mmol) were mixed and heated at 95 ºC for 24 h under nitrogen atmosphere. After cooling the reaction mixture to room temperature and washing with hexane, a yellow viscous ionic liquid IMILCl was obtained.

1.2. Preparation of 1-methyl-3-[(triethoxysilyl)propyl]imidazolium hexafluorophosphate (IMILPF$_6$) and 1-methyl-3-[(triethoxysilyl)propyl]imidazolium tretrafluoroborate (IMILBF$_4$)

A solution of $NaBF_4$ (1.15 g, 10.5 mmol) or KPF_6 (1.93 g, 10.5 mmol) in 30 mL of acetone was added over IMILCl (3.23 g, 10 mmol). The mixture was stirred at room temperature for 6 days and then filtered off. The solvent was evaporated under reduced pressure and the remaining oil extracted in dichloromethane. A yellow viscous liquid was obtained by removing the solvent. The products were labelled IMILPF$_6$ and IMILBF$_4$.

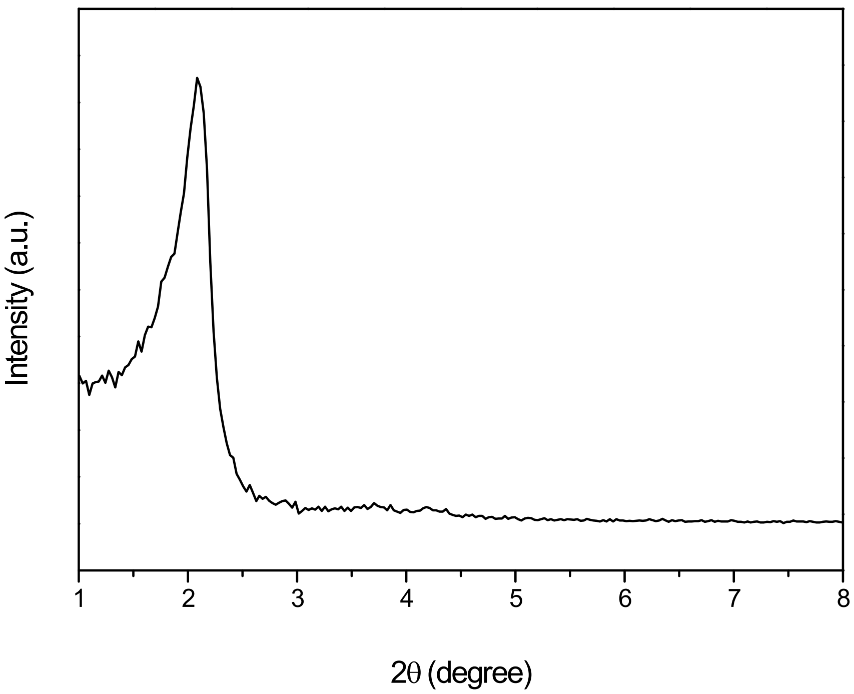


Fig. S1. Small-angle XRD patters of Ti-CoIMILCl-MSN

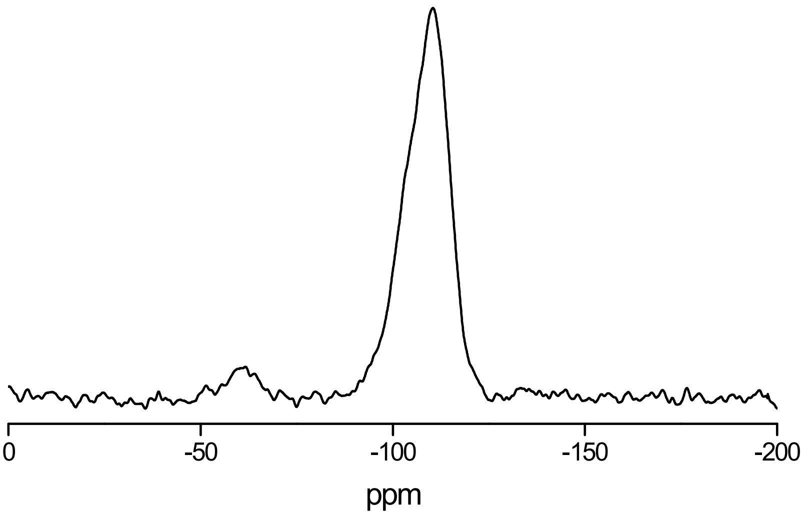


Fig. S2. ^{29}Si CP-MAS NMR spectrum of Ti-IMILCl-MSN

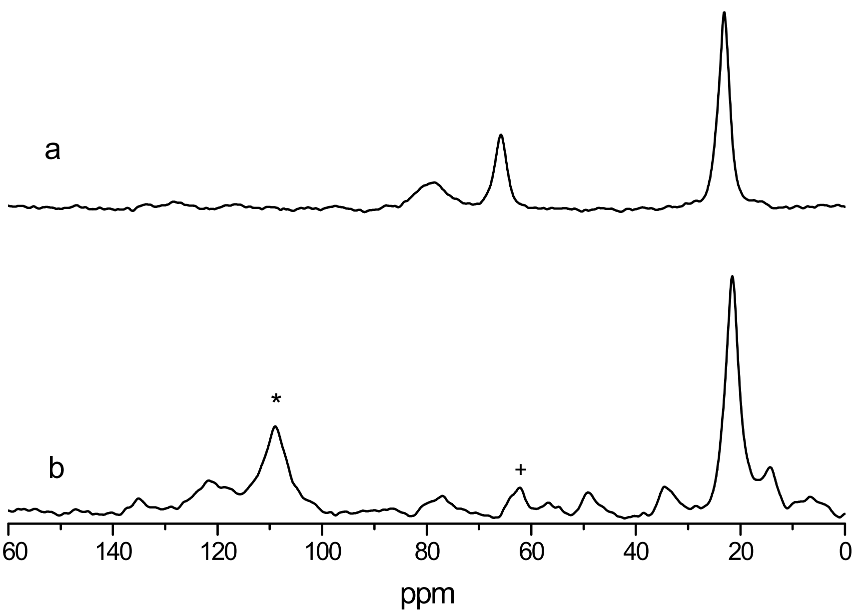


Fig. S3. a) ^{13}C CP-MAS NMR spectrum of 9.45%Ti-MSN and b) ^{13}C PDA-MAS NMR spectrum of 5.4%Ti-CoIMILCl-SiO_2 (*Rotor $^{+}$Sb rotor)

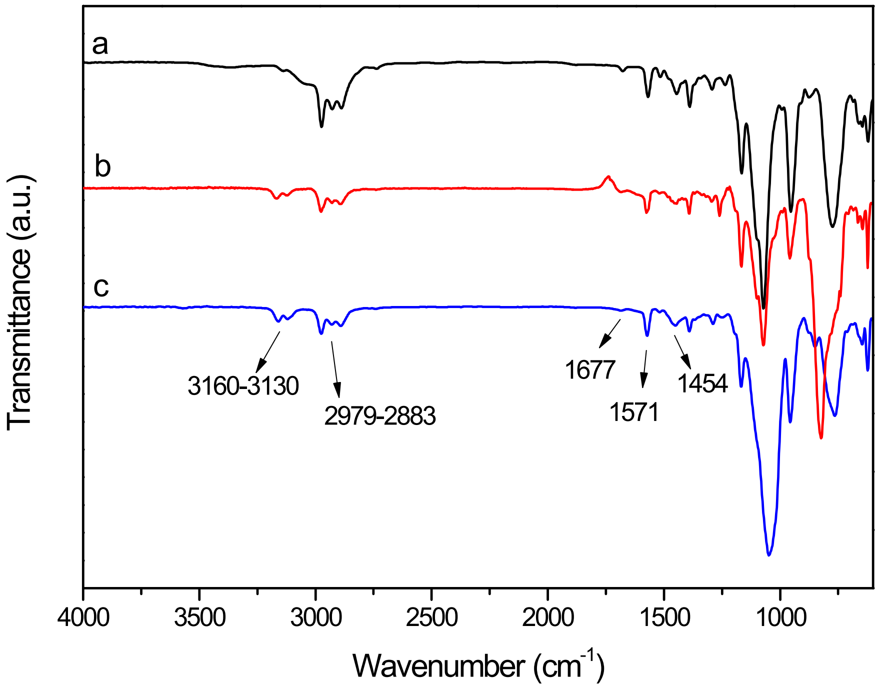


Fig. S4. FT-IR spectra of ionic liquids a) IMILCl, b) $IMILPF_6$ and c) $IMILBF_4$

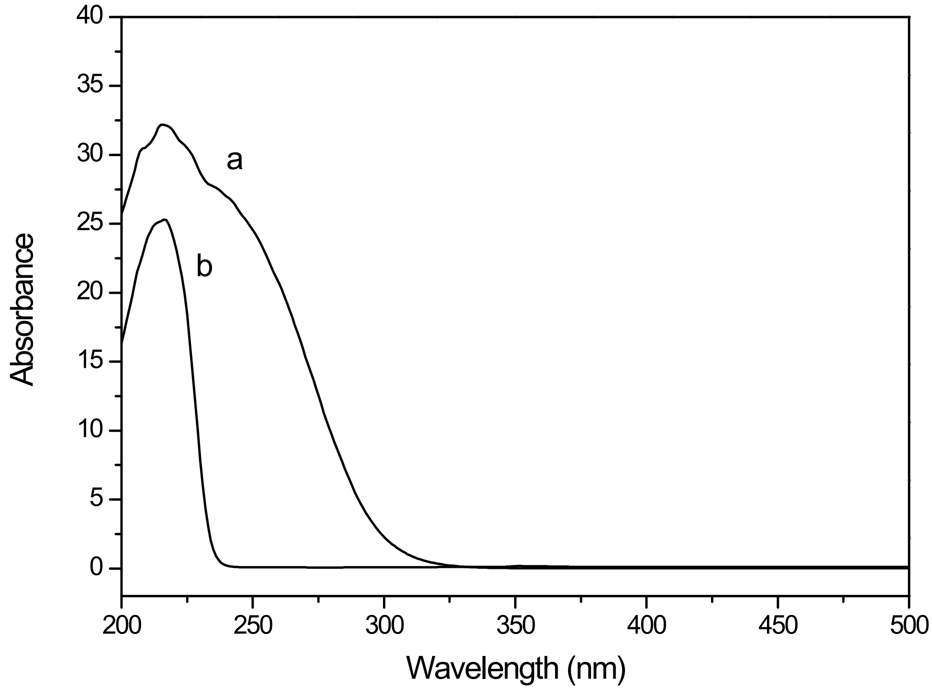


Fig. S5. UV-vis absorption spectra of a) 5.4%Ti-CoIMILCl-SiO_2 catalyst and b) CoIMILCl-SiO_2

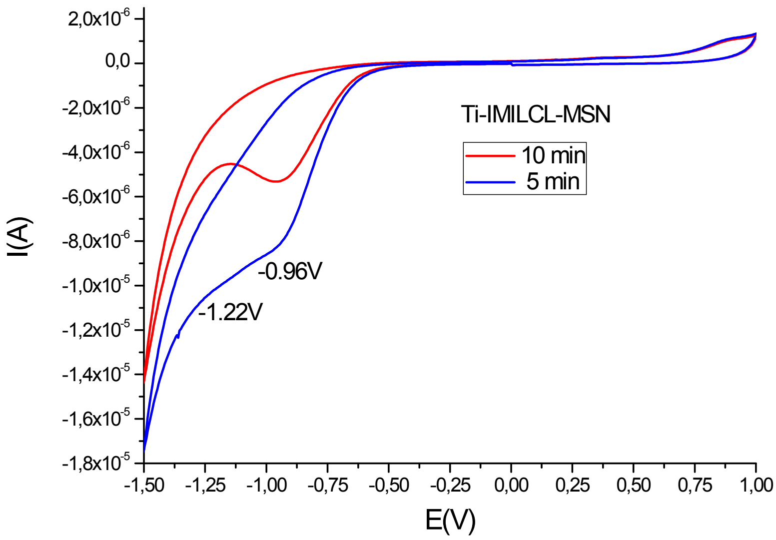


Fig S6. Cyclic voltammogram (scan rate 100 mV s^{-1}) of Ti-IMILCl-MSN at different times after immersion in aqueous phosphate buffer pH 7.4 as electrolyte vs Ag/AgCl/KCl (3M) as reference electrode

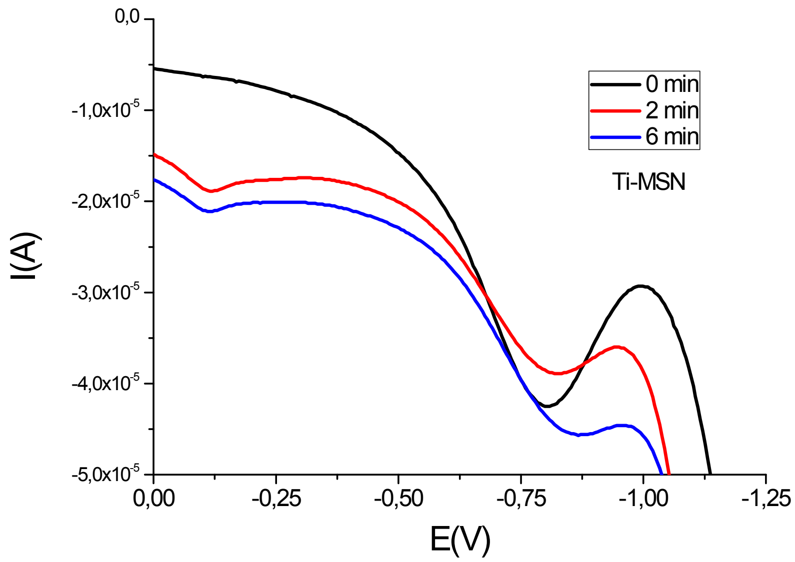


Fig. S7. Differential pulse voltammogram (200 mV modulation amplitude) of Ti-MSN material at different times after immersion in aqueous phosphate buffer pH 7.4 as electrolyte vs Ag/AgCl/KCl (3M) as reference electrode

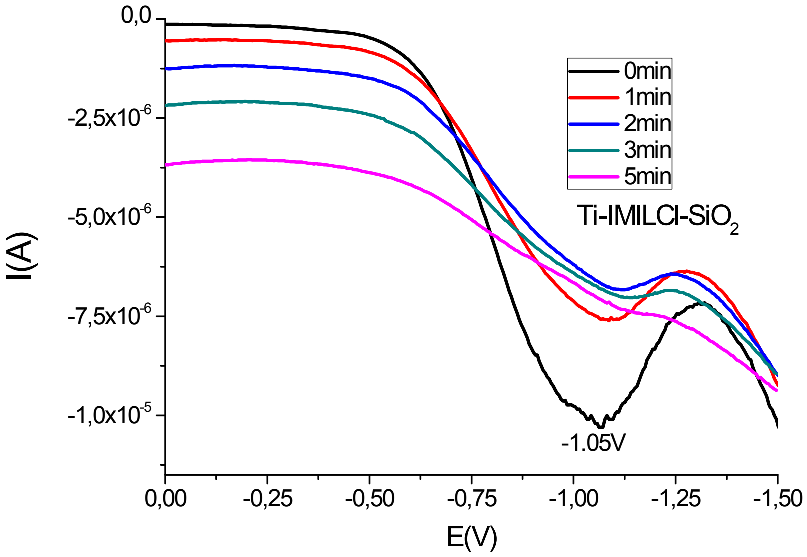


Fig. S8. Differential pulse voltammogram (75 mV modulation amplitude) of Ti-IMILCl-SiO_2 material at different times after immersion in aqueous phosphate buffer pH 7.4 as electrolyte vs Ag/AgCl/KCl (3M) as reference electrode

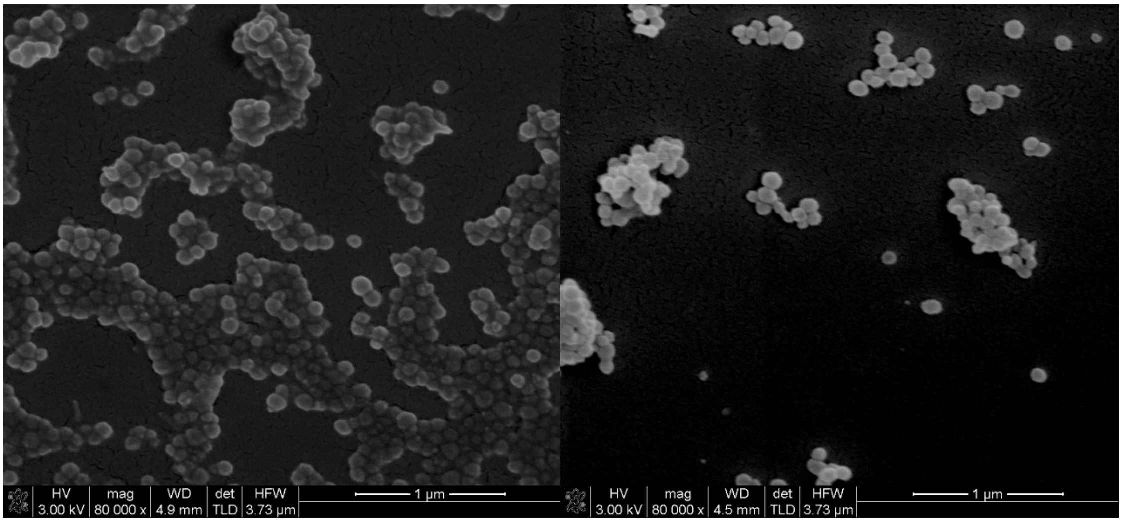


Fig. S9. SEM images of MSN

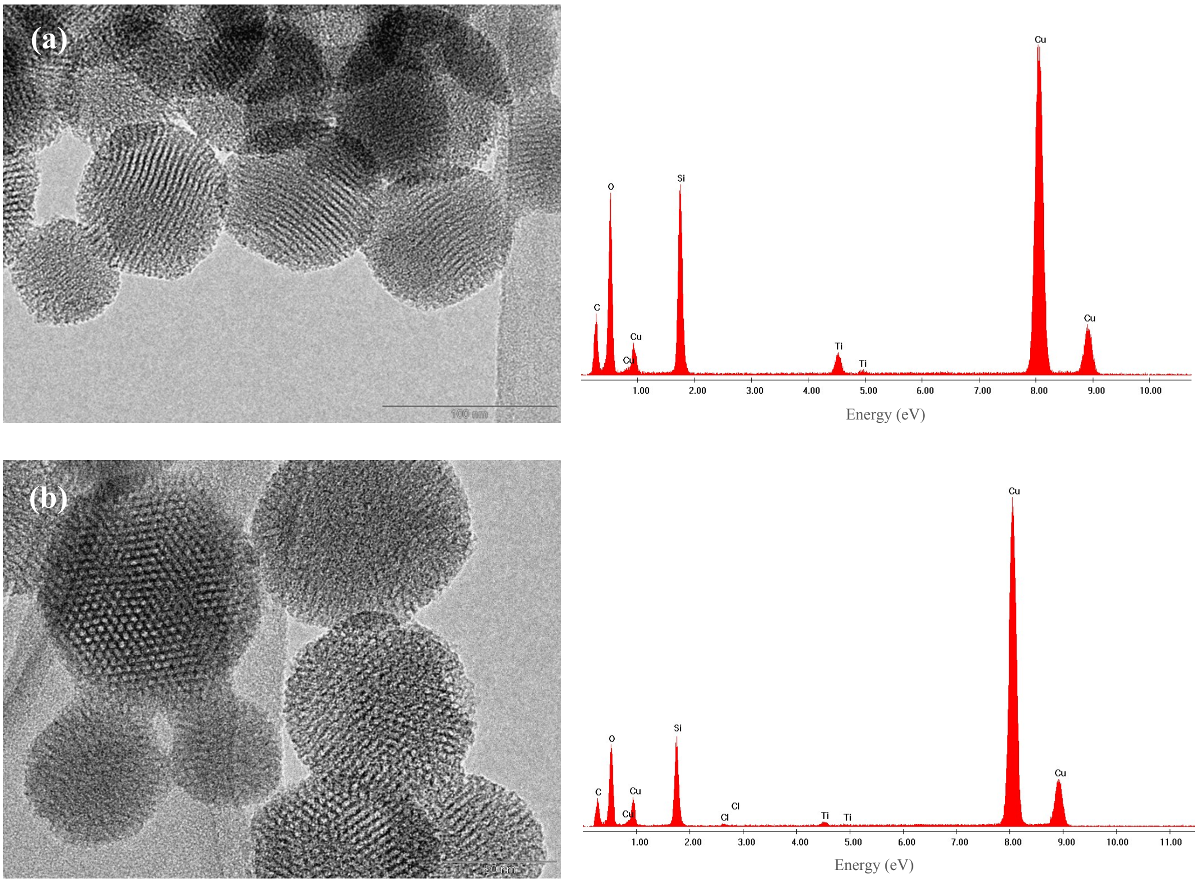


Fig. S10. a) TEM image and EDX spectrum of 9.45%Ti-MSN and b) TEM image and EDX spectrum of Ti-IMILCl-MSN

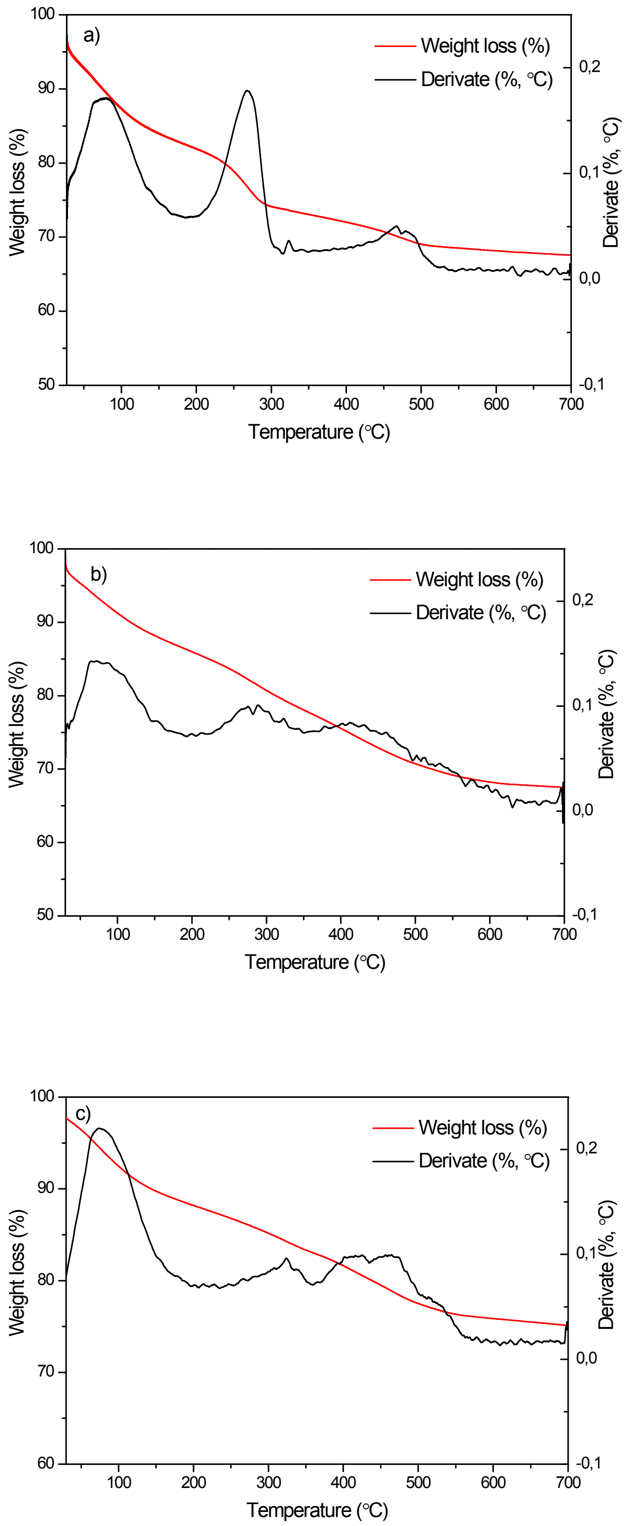


Fig. S11. Thermogravimetric analysis of titanium containing materials a) 9.45%Ti-MSN b) Ti-IMILCl-MSN, and c) IMILCl-Ti-MSN

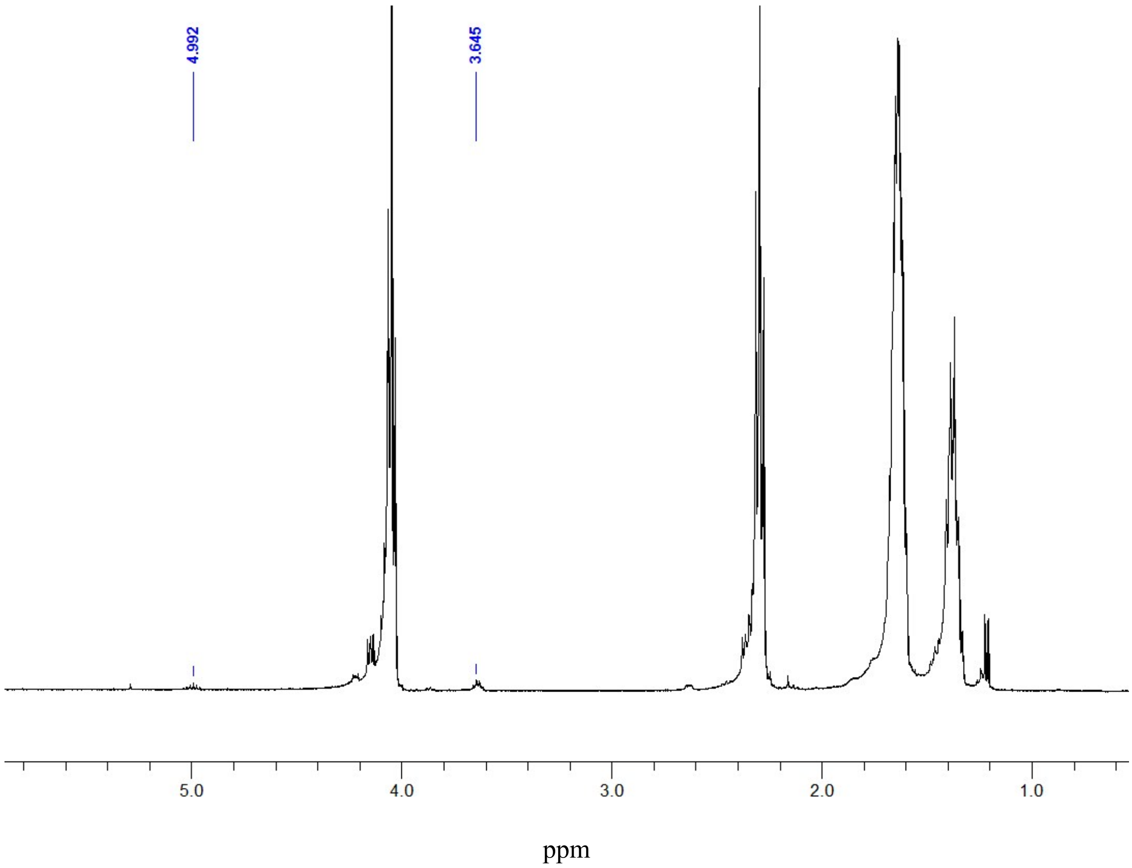
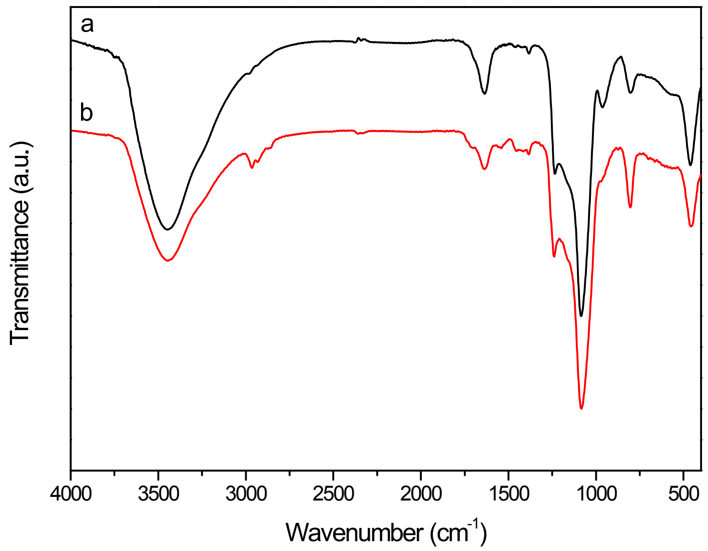


Fig. S12. ¹H NMR spectrum (measured in CDCl3, 400 MHz) of the polymer obtained from the polymerization of ε-CL initiated with Ti-IMILCl-MSN (M_0/I_0 = 100). The proposed coordination insertion mechanism.



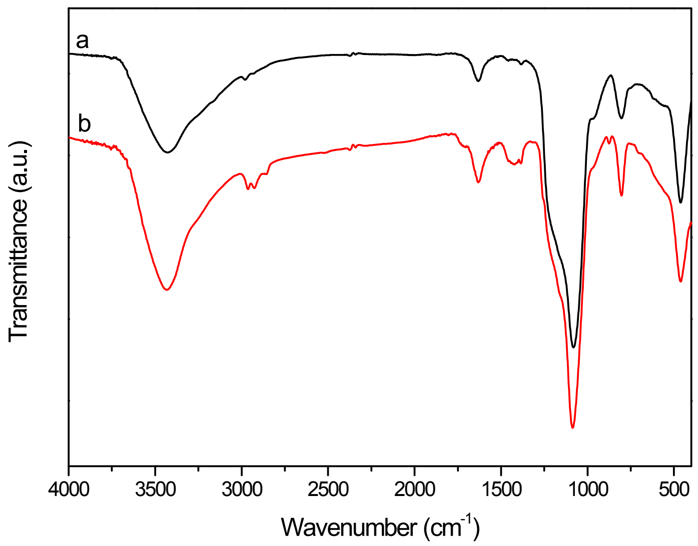


Fig. S13. FTIR spectra of fresh and reused catalysts a) 3.7%Ti-MSN (top) and 3.7%Ti-MSN-R (bottom) and b) IMILCl-Ti-SBA-15 (top) and IMILCl-Ti-SBA-15-R (bottom)

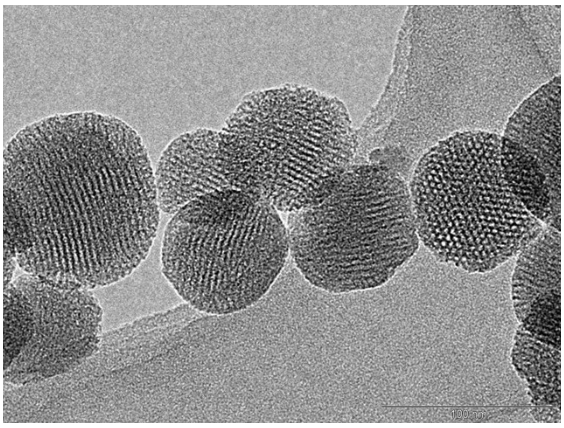


Fig. S14. TEM image of 3.7%Ti-MSN-R

[1] H. Wang, B. Wang, C.-L. Liu, W.-S. Dong, Microporous and Mesoporous Materials 134 (2010) 51–57.