Supplementary Information

"Encapsulated Ionic Liquids (ENILs): From continue to discrete liquid phase" by Jose Palomar,* Jesus Lemus, Noelia Alonso, Jorge Bedia, Miguel A. Gilarranz and Juan J. Rodriguez.

Experimental details

Subsmicrocapsule C_{Cap} synthesis: The carbon submicrocapsules were synthesized by template method**[1]**. A solid core and mesoporous shell aluminosilicate (SCMS) were used as template. The solid core were achieved following the Störb synthesis**[2]**, a volume of 15 mL of tetraethoxysilane (TEOS) was added to a reaction medium formed by 12.6 mL of ammonia aqueous solution (20%, v), 185 mL of ethanol and 20.3 mL of deionized water. The mixture was maintained at 303 K with vigorous stirring during 1 hour to achieve a colloidal solution of silica spheres. A mixture containing 12.5 mL of TEOS and 5 mL of octadecyltrimethoxysilane (C18TMS), was added to the colloidal solution to form the mesoporous shell around them**[3]**. After 1 hour of reaction, the spheres formed were isolated by filtration and calcined at 823 K for 6 h under an air atmosphere. The silica spheres were impregnated by a solution consisting on 0.27 g of Al_36H_2O in 0.3 mL of deionized water. This step was repeated one more time. The powder resulting was dried in air at 353 K and calcined at 823 K for 5 h in air to form SCMS aluminosilicate. A phenol-formaldehyde resin has been used as carbon precursor to obtain carbon submicrocapsules. A mixture of 0.374 g of phenol per gram of template was heated at 373 K for 14 h under 150 mm of Hg static vacuum (rotavapor equipment). Then, 0.238 g of paraformaldehyde per g of SCMS was added and maintain during 24 h under static vacuum at 403 K to obtain a phenol-formaldehyde resin into the SCMS template. This material was heated to 433 K at rate of 1 K/min and held at that temperature for 5 h under a nitrogen flow of 100 NmL/min in a vertical furnace (i.d. 26 mm, length 12 cm). Then, the temperature was raised up to 1123 K with a heat rate of 5 K/min and held at that temperature for 7 h. The resulting carbon aluminosilicate was washed with HF (48%, v) to generate the carbon submicrocapsules.

Incipient wetness: The submicrocapsules (C_{cap}) were filled of IL by means of a direct impregnation, dissolving the IL in acetone. To prevent hydration, IL and acetone were kept in their original tightly closed bottles in a desiccator before use. Impregnation was carried out mixing 1 ml of IL dissolved in acetone for each 100 mg of submicrocapsules. IL concentration in acetone solution was adjusted to obtain different IL loadings on the support. To ensure a homogeneous penetration of the IL solution into the pores, the IL solution was added drop by drop over the surface of the C_{cap}. Then, synthesized ENIL materials were stored at 333 K during 24 h prior to their use. After evaporation of acetone, the ENIL contains from 20 to 83% (w/w) of IL phase.

Characterization: The porous structure of supports and ENIL materials was characterized by means of nitrogen adsorption–desorption isotherms at 77 K using a Micromeritics apparatus (Tristar II 3020 model) and mercury porosimetry using Quantachrome apparatus (PM-3310 model). Before adsorption–desorption experiments, samples were outgassed at 423 K under a residual pressure lower than 10^{-3} Pa. The BET equation was applied to determine the BET surface area (A_{BET}) and Dubinin–Radushkevich equation for micropore volume (0-2 nm). The external or non-micropore area (A_s) was obtained from the t-method. The difference between the volume of N_2 (as liquid) at 0.95 relative pressure and the micropore volume was taken as mesopore volume (2-50 nm). In the mercury porosimetry measurements the estimation of pore diameter from the applied pressure was based on the Washburn equation. The surface tension of mercury was taken as 4.8×10^{-3} N/cm and the mercury contact angle as 141°. The macropore volume was estimated in the 50-100 nm range. Elemental analyses (EA) of C_{cap} and ENILs were carried out in a Perkin–Elmer analyzer (210 CHN model) to obtain C, and N elemental percentages. Thermogravimetric analyses (TGA) of IL and ENIL materials were conducted in a Mettler Toledo Instruments (TGA/SDTA851e model) under nitrogen with a heating rat of 10ºC/min. The accuracy of temperature and mass measurements was 0.1 K and 10^{-3} mg, respectively. A dynamic method was used with a temperature range from 323 to 873 K at a heating rate of 10 K min^{-1} while purging with 50 ml min^{-1} of dry nitrogen. The mass of the sample placed in TGA analyses were between 4 and 12 mg. In all TGA runs, aluminum pans with a capacity of 70 ml were used.

NH_3 capture tests in TGA: Ammonia absorption experiments were carried out in the TGA analyzer at atmospheric pressure and temperatures of 293 and 313 K using 20 mg of IL sample amount. The balance has a weight range of 0–1000 mg with a resolution of 0.1 mg. The temperature of the sample was maintained constant with a regulated external thermostat bath (Huber minisat 125). Gas–liquid-solid equilibrium and kinetic data of ammonia in ENIL materials and neat IL were obtained at 293 K and 0.1 MPa, in a NH_3/N_2 gas flow of 100 N cm^3 /min, 80% (volume) of NH_3 and monitoring the increment on weight of the sample. Desorption experiments were carried out at the absorption temperature and pressure under dry nitrogen flow (100 N cm^3 /min).

NH_3 capture tests in fixed-bed column: The sorption of ammonia was also evaluated in a continuous flow system, which consists of a quartz fixed-bed column (1/4 inch diameter), coupled to a quadrupole mass analyzer (OmniStar/ThermoStar). Experiments were conducted under following operating condition: 293K of temperature, 2000 ppmv of inlet ammonia concentration, 20 N cm^3 /min of gas flow, atmospheric pressure and 8 cm of height of adsorbent/absorbent material (C_{cap}, ENIL-R_2 and ENIL-R_4). Ammonia detection was carried out utilizing a single quadrupole mass analyzer. The signal selected in order to quantify the amount of NH_3 in the gas outlet of the reactor was an ion current of 14.98A. Desorption experiments were performed after 50 minutes of NH_3 sorption on ENIL materials. A N_2 flow of 20 N cm^3 /min was passing through the column with the exhausted ENIL materials at 293 K,

during 30 minutes and then the temperature was raised at 343 K during 20 minutes and 0.1MPa for the completed regeneration. The regenerative cycles were conducted three times.

REFERENCES

1 Yoon, S. B. and Sohn, K. and Kim, J. Y. and Shin, C. and Yu, J. , Hyeon, T., *Adv Mater,* 2002, *14,* pp. 19-21.
2 Stober, W. and Fink, A., Bohn, E., *J.Colloid Interface Sci.,* 1968, *26,* pp. 62.
3 Buchel, G. and Unger, K. K.and Matsumoto, A., Tsutsumi, K., *Adv Mater,* 1998, *10,* pp. 1036.

Figure S1 (a) Nitrogen adsorption-desorption isotherms at 77K and (b) Pore size distribution (6 to 100nm) from Hg porosimetry of carbon submicrocapsules (C_{Cap}) and encapsulated ionic liquid (ENIL-R_n) materials with increasing amounts of $OmimPF_6$ (0-80% w/w).

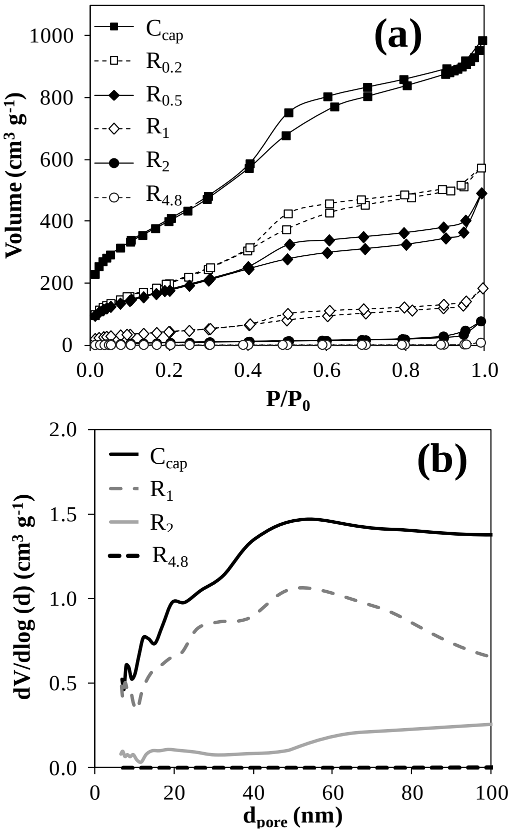

Figure S2 Normalized derivative thermogravimetric curves (DTG) obtained under nitrogen atmosphere at a heating rate of 10 ºC/min, for $EtOHmimBF_4$ and ENIL-R_n materials prepared with different amount of this IL.

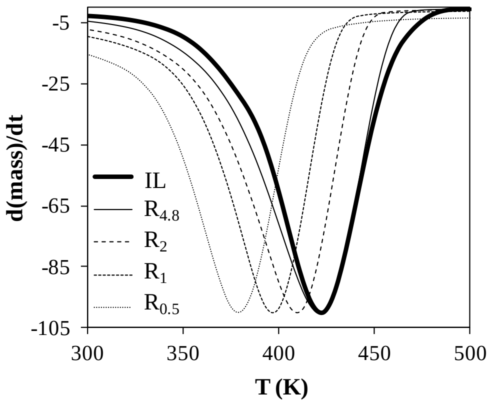

Figure S3. Sorption-desorption breakthrough curves of NH_3 capture obtained with ENIL-$R_{4.8}$ in fixed-bed column tests.

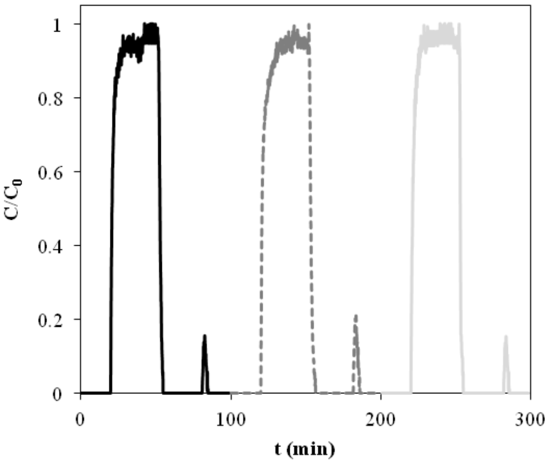

Table S1. Results of NH_3 capture with the ionic liquid (IL) $EtOHmimBF_4$ and ENIL-R_n materials prepared with this IL obtained in thermogravimetric tests at 293 K, 1 atm and 0.08 MPa NH_3 partial pressure, where the ammonia absorption capacity of IL-based system is expressed per unit mass of IL.

	Thermogravimetric tests		
	Pseudo-second order model		
	$\frac{t}{q_t} = \frac{1}{kq_s^2} + \frac{t}{q_s}$		
	$\boldsymbol{q_s}$	$\boldsymbol{k}$	$\boldsymbol{R^2}$
IL	101	$3.5 \cdot 10^{-3}$	0.999
ENIL R_2	106	$7.1 \cdot 10^{-3}$	0.998
ENIL $R_{4.2}$	104	$12.8 \cdot 10^{-3}$	0.999
q_s ($mg \cdot g^{-1}$); k ($mg \cdot g^{-1} \cdot min^{-1}$)			

Table S2. Results of NH_3 adsorption-desorption with ENIL-R_4 material obtained in fixed bed reactor tests at 293 K, 2000 ppmv of inlet ammonia concentration, 20 N cm^3 /min of gas flow, atmospheric pressure in bed column of 8 cm of height and 1/4 inch diameter.

Cycle	**$t_{0,5}$ (min)**	**q_s ($mg \cdot g^{-1}$)**	**q_s ($mg \cdot cm^{-3}$)**
1	20.4	1.85	0.22
2	19.8	1.80	0.21
3	20.2	1.83	0.22