

## SUPPLEMENTARY MATERIAL

### PYROLYSIS STUDY OF THE SILICA/ALGINATE IMMOBILIZATION MATRIX

#### Thermal and mass spectrometric analysis

To a deeper knowledge of the chemical composition of the both the alginate and silica counterparts, a specific and detailed thermal analysis was carried out on sample **5**, which is the best performing. Before the analysis, it was dried at 90 °C for 5 days and at 120 °C for 36 hours. Pyrolysis was carried out on 14.4 mg. TG curve showed (Fig. 1 S.M.) a continuous mass loss up to 840 °C with a total intensity of 61.1 wt % divided in three main events in the 80÷405, 405÷565, 565÷840 °C intervals, with relative intensity 40.0, 7.9, 10.0 wt %, respectively.

DTA analysis showed an initial exothermic peak at the beginning of the first thermogravimetric event, rapidly converted into a more pronounced endothermic process in the following part. Small endothermic processes were also detected for the two remaining thermogravimetric events.

Mass spectrometric TIC curve showed an intense peak centred at 273 °C followed by two smaller bands at 480 and 738 °C. The first TIC peak corresponded to the mass spectra of the intense pattern signal of CO<sub>2</sub> ( $m/z$  44, 28) and, in less extent, of H<sub>2</sub>O ( $m/z$  18, 17, 16). For the TIC band at 738 °C, mass spectra showed the only presence of CO<sub>2</sub>; while, in the middle band together with the signal pattern of CO<sub>2</sub> and H<sub>2</sub>O, several other signals up to  $m/z$  106 were revealed. This more complex picture could agreed with the presence of a mixture of light saturated hydrocarbons, mainly methane ( $m/z$  14-16), ethane ( $m/z$  26-30), propane ( $m/z$  38-44), and in less extent, butane ( $m/z$  51-58) and unsaturated species such as benzene ( $m/z$  77, 78), toluene ( $m/z$  91, 92) up to dimethylbenzene ( $m/z$  105, 106).

IC curves of appropriate  $m/z$  signal, extrapolated from the TG-MS analysis, allow monitoring the release of single species during the entire pyrolysis. The trend of  $m/z$  18 ion current (used to detect H<sub>2</sub>O release) showed an intense asymmetric band (maximum at 252 °C), with a tailing effect, and a small band at 488 °C, which was in correspondence with the second thermogravimetric event. The ion current of  $m/z$  44 signal indicated the evolution of CO<sub>2</sub>; this trend presented an intense band

centred at 274 °C followed by a small plateau up to 425 °C, and a second important band at 730 °C, in agreement with the third TIC band. The sum of all other fragmentation ions (detected in the mass spectra recorded inside the second TIC band and not correlated to CO<sub>2</sub> and H<sub>2</sub>O) afforded an ion current curve with a symmetric intense band centred at 484 °C, according to the second TIC band. This last curve is used to monitor the cumulative evolution of the hydrocarbon species.

### **Semi-quantitative evaluation of TG-MS data**

A semi-quantitative evaluation of CO<sub>2</sub>, H<sub>2</sub>O and of hydrocarbon mixture, was obtained taking into account TG-MS data according to a well-proved procedure reported elsewhere [1 SM; 2 SM]. The 14.4 mg of sample, released  $1.14 \times 10^{-4}$ ,  $6 \times 10^{-6}$  and  $6.4 \times 10^{-5}$  mol of CO<sub>2</sub> respectively during the I, II and III thermogravimetric event;  $4.1 \times 10^{-5}$  and  $2 \times 10^{-6}$  mol of H<sub>2</sub>O were evolved in the I and II event. In the second mass loss,  $8.2 \times 10^{-4}$  g of hydrocarbons species was released (in reason of 71.7 wt % of this event). These amounts were calculated by considering: (i) the relative intensity of all *m/z* signals present in the mass spectra of H<sub>2</sub>O and CO<sub>2</sub>; (ii) the integrated values of the single bands present in both the IC and TIC curves; (iii) the relative and total mass losses recorded in the TG analysis; (iv) the correlation factor between the sensibility of the mass spectrometric detector and the absolute value of the mass loss, which is firstly calculated for CO<sub>2</sub> during the third TG-event and then for the H<sub>2</sub>O signal.

### **Pyrolysis interpretation.**

Several attempts were made in order to fit the experimental TG-MS results with the chemical composition attributed to the dried **5** sample. The best data-fit was carried out by separately comparison of the mass balance deduced by the chemical composition, assumed for the residual solid after the TG analysis, and the amounts of the species released as gas phase during pyrolysis, detected by MS measurements. This fit leads to consider the sample formed by total substitution of Na<sup>+</sup> cations, originally coordinated to the  $-\text{[C}_6\text{O}_6\text{H}_7^-]_n-$  polymeric units of the starting alginate

solution, with the hemi-stoichiometric amount of  $\text{Ca}^{++}$  ions, introduced during gelling process of the alginate beads. In fact, the presence of  $\text{Ca}^{++}$  was responsible for the cross-linking of the linear alginate chains. The third TG event as exclusively been due to the decomposition of  $\text{CaCO}_3$ , quantitatively formed in the previous pyrolysis steps and arising from the carboxylic moieties coordinated to  $\text{Ca}^{++}$  cations in the alginate matrix.

From  $^{29}\text{Si}$  NMR result, (see RESULTS AND DISCUSSION, sample obtained by **Method A**), the inorganic matrix was described by the nominal composition  $(\text{OH})_{0.427}\text{SiO}_{1.786}$ . Accordingly, the 14.4 mg sample was constituted of  $3.26 \times 10^{-5}$  mol of  $-\text{[C}_6\text{O}_6\text{H}_7^-\text{Ca}^{++}\text{C}_6\text{O}_6\text{H}_7^-]_n-$  cross-linked units, coated by  $2.63 \times 10^{-5}$  mol of  $-\text{[(OH)}_{0.427}\text{SiO}_{1.786}]_m-$  silica gel units. This result allowed quantifying the efficiency of the silica deposition in 11.7 wt %. After pyrolysis up to 1000 °C, the recovered solid (5.6 mg) was constituted by  $3.26 \times 10^{-5}$  mol of CaO,  $2.63 \times 10^{-5}$  mol of  $\text{SiO}_2$  and  $1.821 \times 10^{-4}$  mol of graphitic-carbon. During the pyrolysis it may be supposed that the 12 carbons of the alginate unit produced about 4 (i.e.= 4.7) evolved  $\text{CO}_2$  molecules and about 5 (i.e.= 5.6) graphite carbons; the two remaining carbons (i.e.= 1.7) account for hydrocarbons released in the 400-550 °C interval. A reliable justification for the minor evolution of aromatic hydrocarbon (less than 0.3 C atoms of the original 12 in the alginate structure) can not be advanced and probably requires a dedicated work. Here the presence over xerogel silica at 480 °C may induce particular catalytic pathway for the alginate network degradation. As for the total  $\text{H}_2\text{O}$  release ( $4.32 \times 10^{-5}$  mol),  $5.6 \times 10^{-6}$  mol may arisen from the condensation of  $\equiv\text{Si}-\text{OH}$  groups of the silica gel, and  $3.76 \times 10^{-5}$  mol from the condensation of  $\equiv\text{C}-\text{OH}$  of the alginate. This fact implies that almost all the hydroxyl groups (ca. 87%) of the hemiacetal-ring undergo condensation during the first pyrolysis step.

The reliability of the original chemical composition and the proposed pyrolysis mechanism were confirmed by the balance ( $\pm 3\%$ ) between oxygen atoms, remaining in both the solid residue and the released gaseous  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (mass-spectrometric-detected), in comparison with those contained in the initial **5** sample (thermogravimetric-detected). Anyway, a 5% error was obtained

considering the mass balance between total weight losses (TG-detected) and calculated mass of all evolved gases (MS-detected).

#### **SUPPLEMENTARY MATERIALS BIBLIOGRAPHY**

[1 SM] R. Campostrini, M. Ischia, L. Palmisano. Pyrolysis study of sol-gel derived TiO<sub>2</sub> powders - Part I. TiO<sub>2</sub> - anatase prepared by reacting titanium (IV) isopropoxide with formic acid. *J. Therm. Anal. Cal.*, 2003, **71**, 997-1009

[2 SM] G. Carturan, R. Campostrini, L. Tognana, S. Boninsegna, R. Dal Toso, R. Dal Monte R. Gas-Phase Silicon alkoxide reactivity vs Na-alginate droplets for conjugation of Alginate and sol-gel Technologies. *J. Sol-Gel Sci. Technol.*, 2006, **37**(1), 69-77.

## SUPPLEMENTARY MATERIALS FIGURE

Figure 1 SM. TG-MS analysis of sample 5. Insets show the mass spectrum of main peaks of the TIC curve.

