

High-Density Energetic Material Hosted in Pure Silica MFI-Type Zeolite Nanocrystals**

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Desensitization, that is, the reduction of the sensitivity of energetic materials, has been an essential subject of interest since the discovery of energetic materials and continues to be important nowadays. Prime examples of such materials are black powder and dynamite, which are desensitized potassium nitrate and nitroglycerine, respectively. Thus, desensitizing these compounds is of great importance not only to enhance their safe use, but also to make them less dangerous in fields such as the production of standards for analytical purposes and the detection of explosive devices.^[1–3] Ideally, the desensitized energetic materials, depending on their intended use, should possess properties similar to those of the pure compound, including spectral and thermal properties, while avoiding hazards such as friction, heat, and shock sensitivity.^[4]

One of the traditional ways to desensitize crystalline high-energy materials is to press and knead them into a form with the help of binders and plasticizers to shape plastically bonded explosives.^[5] Other procedures include mixing the energetic materials with inert substances such as salts or oil,^[6,7] or coating with waxes or plasticizers,^[8,9] and additionally regulating the oxygen balance with the help of nonexplosive nitrocompounds.^[10] However, these procedures sometimes cause problems at different stages of the manufacturing process, for instance during dry mixing or blending at elevated temperatures. Furthermore, some of the additives for desensitizing/plasticizing also raise environmental concerns and increase the cost considerably. Thus developing a safe, cost-effective, and environmentally friendly way to desensitize crystalline highly energetic materials is of great interest. Besides, there is an escalating need for detection of sensitive energetic materials used in improvised explosive devices with safety issues as the main concern.

Inclusion chemistry in framework-type materials has shown an effective tailoring of some of the physicochemical proper-

ties of molecules and compounds through orientation and/or conformation inside the porous networks.^[11] The incorporated materials usually exhibit properties that differ from those in the pure solid or solution phases; they may even display some properties that cannot be achieved in either of these, such as nonlinear optical responses for second-harmonic generation and micro-antenna applications.^[12,13] For inclusion chemistry, the unique pore structure of crystalline zeolite-type materials based on tetrahedrally coordinated silicon and aluminum is very attractive. These materials offer large pore volume and great internal and external surface areas with variable pore openings and apertures. Such structures make it possible for so-called guest molecules, either neutral or charged, to penetrate and leave the porous structure by diffusion processes.

The lifetime of various labile species and molecules incorporated in zeolites has been described in the open literature,^[14] but not the thermal decomposition, which in the case of high-energy materials is of extreme importance. The use of zeolites in connection with high-density energetic materials to date has been restricted to vague ways to reduce the toxicity of the gases produced upon decomposition,^[15] and as a filling material for mixtures of nitrates.^[16]

The objective of the work reported here is to apply nanometer-sized microporous crystals with a regular pore system to immobilize high-density energetic materials, and to demonstrate the stabilization role of the porous host in the preparation of safe standards for diverse detection purposes. Moreover, it is important to note that all the desensitizing procedures for energetic materials reported up to now are not aimed at detection purposes. The system presented here allows not only the stabilization of highly energetic compounds, but also the creation of standards for possible identification based on spectroscopic techniques.

For the current study, a pure silica zeolite with MFI-type structure with nanometer-sized dimensions was chosen in order to achieve high loading with the energetic material through fast diffusion, and to keep some remaining vapor pressure for further investigations on other compounds that rely heavily on it for their detection through dogs and spectrometry techniques.^[1–3] It is anticipated that the MFI zeolite with its three-dimensional channel network will be able to include high-energy materials and separate them into localized domains, and thus will delay or hinder a chain reaction that would eventually lead to an explosion. Also, the MFI network, consisting of intersecting straight and sinusoidal channels occupied by the energetic materials, would be able to control an exothermic reaction in a way that the net local

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pressure caused by decomposition or explosion will be absorbed by the zeolite network. In this way the propagation of an explosion, which is a diffusion-controlled reaction, can be hindered by domain formation and energy redirection to the zeolitic inorganic structure. Moreover, the inclusion of the energetic material in the channels of zeolite crystals would diminish their friction strain, which is an extremely important feature for sensitivity issues.

The high-energy material used in this work is 1,1-diamino-2,2-dinitroethylene (Fox-7), which is a high-performance compound with properties close to those of trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX) but with lower sensitivity in comparison to TNT.^[17,18] Besides, Fox-7 has attracted considerable attention because it decomposes into CO₂, N₂, and H₂O, making it an ideal “green” high-density energetic material that does not produce solid deposits or toxic gases.

Fully crystalline MFI samples obtained under hydrothermal treatment were purified, freeze-dried, and calcined prior to immobilization of Fox-7 in either acetone or acetone/dimethyl sulfoxide (DMSO) mixtures. Only the Bragg reflections typical of the MFI zeolite were present in the X-ray diffraction (XRD) patterns; no reflections belonging to the pure Fox-7 compound were identified even in the samples treated with highly concentrated solutions (Fig. 1). The morphology and size of pure MFI samples and those treated with Fox-7 are similar, that is, discrete round-shaped crystals about 100 nm in size, and no impurities between the zeolite particles (scanning electron microscopy images are not shown).

The immobilization of Fox-7 in the porous nanocrystals is verified by the Raman spectra recorded from samples F-Sil-50, F-Sil-30, and F-Sil-10 with different concentrations of Fox-7 in comparison with the pure compounds (Fig. 2). The spectra of the samples are dominated by the vibrations characteristic of Fox-7, and only the weak band at 381 cm⁻¹ is zeolitic-structure sensitive. A slight change in the intensities of the bands at 1343 and 858 cm⁻¹—associated with symmetric C–NO stretch/NH wagging and NO/NH rocking vibrations,

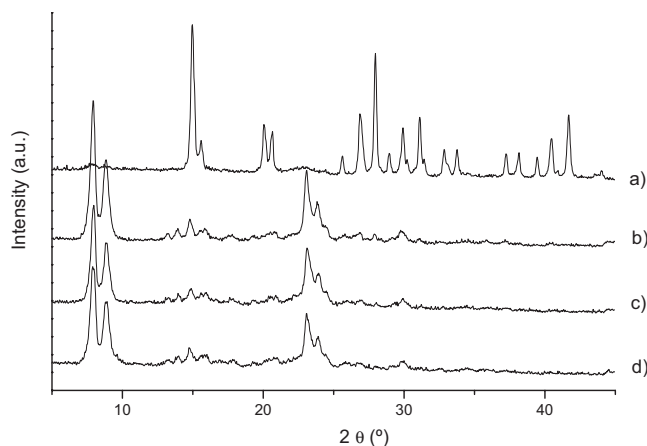


Figure 1. XRD patterns of a) pure Fox-7, b) F-Sil-50, c) F-Sil-30, and d) F-Sil-10 samples.

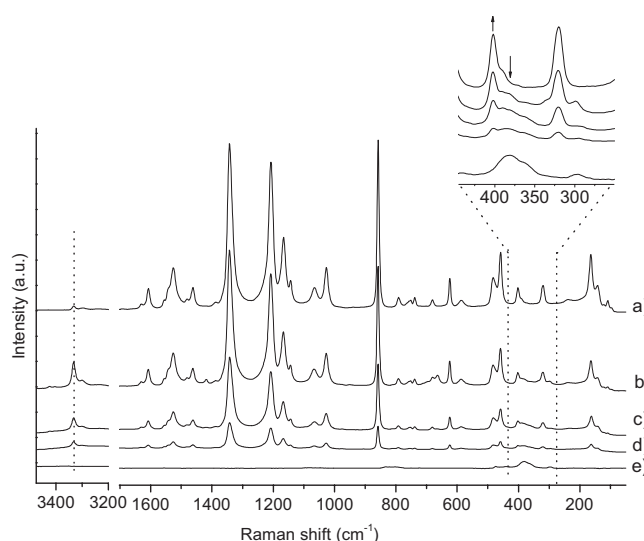


Figure 2. Raman spectra of a) pure Fox-7, b) F-Sil-50, c) F-Sil-30, d) F-Sil-10, and e) pure MFI samples; the inset shows the spectra in the range of 250–500 cm⁻¹.

respectively—is observed in the spectra of the treated MFI samples (Fig. 2b–d).^[19] More pronounced is the strong increase in intensity of the band at 3332 cm⁻¹, which is assigned to asymmetric NH stretching, indicating a state of disordered hydrogen bonds unlike in the pure Fox-7 (Fig. 2a). This observation is also supported by temperature-dependent study of the phase transitions of pure Fox-7.^[20] In general, the intensity of the vibrations originating from Fox-7 increases noticeably with increased loading of the zeolite samples. The inset in Figure 2, showing the region between 250 and 500 cm⁻¹, verifies the change in the intensities of the double-five-ring vibration mode (381 cm⁻¹) and the asymmetric NH wagging band coming from Fox-7 (407 cm⁻¹). With increasing loading of Fox-7 in the MFI host, the former band disappears, while the second one shifts to higher wavenumber, and increases in intensity due to the partial overlapping of the two bands. Additionally, the duration and temperature of treatment did not play an important role in the inclusion of Fox-7 in the zeolite hosts.

Additional increase in the loading and stabilization of Fox-7 can also be achieved by coordination of the target molecule to metal centers that are included in the zeolite framework. Quantum chemical calculations for Fox-7 show good interaction with aluminum centers,^[21,22] and thus the inclusion of high-energy materials is expected to be improved in the Al-containing ZSM-5 zeolite. The inclusion degree of Fox-7 in Al-containing MFI-type nanocrystals is under investigation.

In addition to Raman spectroscopy, solid-state ¹³C NMR was used to study the occluded Fox-7 in the MFI nanocrystals and compared with the pure compounds (Fig. 3). The MFI sample was initially prepared in the presence of tetrapropylammonium hydroxide (TPAOH) as a template, and prior to immobilization of Fox-7 the TPAOH was removed by means of calcination. The signals coming from TPA⁺ in the initial MFI samples appear at 66.3 ppm, 17.9 ppm, and a split signal

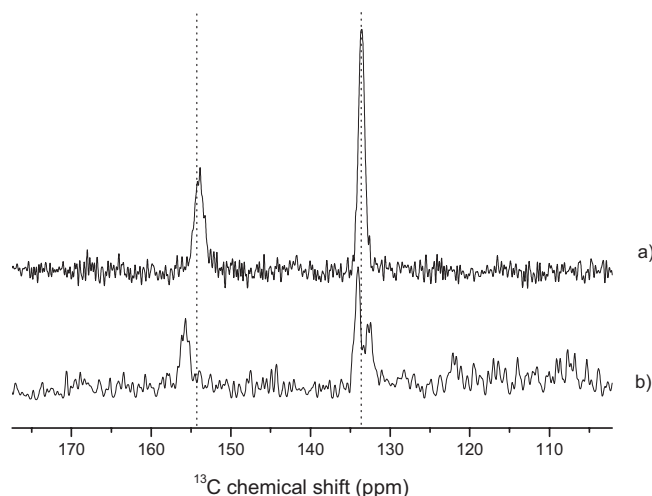


Figure 3. ^{13}C magic angle spinning NMR (MAS NMR) spectra of a) pure Fox-7 and b) F-Sil-50; ^{13}C NMR spectra were recorded at 125.787 MHz, spinning rate 6 kHz, with pulse lengths of 10.0 μs and 5 μs for pure Fox-7 and F-Sil-50, respectively.

at 12.5 ppm and 11.5 ppm.^[23] The original band at 10.3 ppm generated by the methyl carbon splits into two components, which are associated with CH_3 groups located in the two types of channels, that is, straight and sinusoidal, of MFI-type materials. The $=\text{C}-(\text{NO}_2)_2$ signal of pure Fox-7 in solution is at 158.8 ppm^[17] and that in the solid state appears at 153.8 ppm, while in our case the signal is located at 155.6 ppm (Fig. 3). This shift can be related to the disorder of the included Fox-7 molecules already observed in the Raman spectra. As has been observed, there is a torsion of the $\text{C}-\text{NO}_2$ bond in the pure crystalline Fox-7; this is not present in solution and it is minimal in our case.^[20] Early investigations on the splitting of the $=\text{C}-(\text{NH}_2)_2$ signal (134.24 and 132.73 ppm) point towards a coordination of the amine moiety to the zeolite framework. In addition to the shifting of the peaks, a broadening is observed due to the different surroundings of Fox-7 in the host materials. The ^{13}C NMR spectra in combination with the Raman data clearly demonstrate the immobilization of Fox-7 in the zeolite nanocrystals.

Once the presence of Fox-7 in the zeolite hosts had been verified, the most interesting features of this high-energy material were followed with differential scanning calorimetry (DSC), enabling us to explore the exothermic properties of energetic materials safely.^[20] A striking change in the two exothermic maxima is observed for Fox-7 incorporated in samples F-Sil-50, F-Sil-30, and F-Sil-10 in comparison with pure unsupported compound (Fig. 4). The first peak in the spectra of zeolite samples containing Fox-7 shifts about 30 °C higher, that is, to 264 °C, and the second one almost 100 °C, that is, to 377 °C. For assessment, the exothermic features of pure Fox-7 with a first exotherm at around 225 °C and the explosive decomposition beyond 275 °C can be seen in the DSC plot (Fig. 4d); the DSC curve of pure Fox-7 has been down-

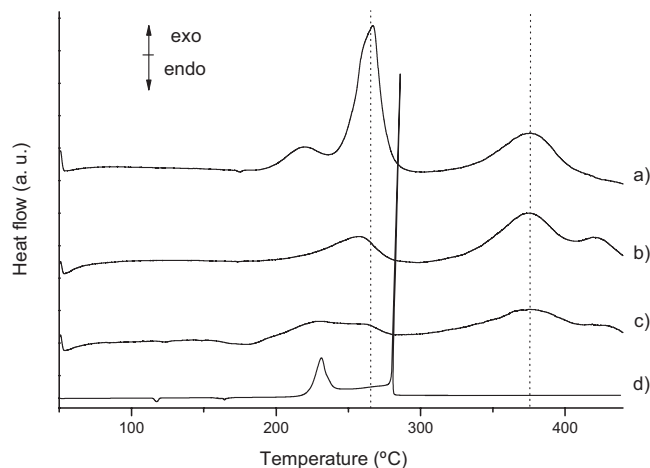


Figure 4. DSC curves of a) F-Sil-50, b) F-Sil-30, c) F-Sil-10, and d) pure Fox-7. The dotted lines mark the peaks at 265 and 376 °C.

scaled 20 times due to the high-intensity explosive decomposition beyond 275 °C.

Additional differential thermogravimetry (DTG) measurements were carried out in order to verify the maximum loading amount of samples F-Sil-30 and F-Sil-50 with Fox-7. Samples F-Sil-30 and F-Sil-50 contain about 6.0 and 13.5 wt % of Fox-7, respectively (for the calculations only the weight loss above 178 °C was taken into consideration to avoid possible residual solvent contributions).

In conclusion, the successful immobilization of a high-density energetic material (Fox-7) inside MFI-type nanometer-sized zeolites is demonstrated. A marked stabilization of Fox-7 leading to a nonexplosive decomposition about hundred degrees above the explosive temperature for the pure substance is achieved. Moreover, the immobilization of energetic materials in zeolite hosts has been proved to thermally stabilize the compounds, which opens new possibilities for preparation of safe standard materials for detection.

Aside from the thermal and mechanical stability that the nanometer-sized porous hosts can provide, they also possess low spectral profiles in techniques such as Raman, ^{13}C NMR, and mass spectrometry, which are the techniques currently used for detection of explosives in post-explosion debris. These qualities make nanometer-sized porous materials exceptional candidates for host systems aimed at detection of highly sensitive guest molecules. Thus the immobilization of energetic materials in nanometer-sized porous matrixes can assure the desired stabilization of the high-energy materials, and still show the desired spectrometric properties.

Experimental

Nanometer-sized MFI-type zeolite was synthesized from pure silica solutions with the following composition: 25 SiO_2 : 9 TPAOH: 420 H_2O : 100 EtOH. The clear solution was converted into a crystalline suspension by heating at 90 °C for 4 days. The purified, dried, and

calcined zeolite was used for inclusion of Fox-7 provided by NEXPLO (Bofors, Sweden) in wet form; prior to use it was dried at 50 °C for 3 h. Fox-7 was dissolved in acetone or acetone/DMSO mixtures for safe inclusion in the nanometer-sized microporous crystals under stirring at room temperature (RT) for 6 h. The nanometer-sized crystals were separated from the solutions by centrifugation, washed with pentane, and dried at RT. The crystalline structure of the porous hosts before and after immobilization of Fox-7 was determined from powder XRD patterns. Information about the crystal size and morphology of the porous materials was obtained by scanning electron microscopy and dynamic light scattering. The presence of Fox-7 in the MFI nanometer-sized crystals was traced with Raman and NMR spectroscopy, DSC, and DTG. The zeolite samples are named according to the amount of Fox-7 used for inclusion as the weight percentage of the dry zeolite. Samples F-Sil-50, F-Sil-30, and F-Sil-10, respectively, correspond to zeolites treated with 50, 30, and 10 wt % Fox-7 in relation to the weight of the zeolite used.

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- [1] J. I. Steinfeld, J. Wormhoudt, *Annu. Rev. Phys. Chem.* **1998**, 49, 203.
[2] D. W. Hannum, J. E. Parmeter, *Survey of Commercially Available Explosives Detection Technologies and Equipment*, Sandia National Laboratories, Albuquerque, NM **1998**.
[3] A. M. Rouhi, *Chem. Eng. News* **1997**, 75 (39), 24.
[4] D. M. Hoffman, B. J. Cunningham, T. D. Tran, *J. Energ. Mater.* **2003**, 21, 201.
[5] J. Akhavan, *The Chemistry of Explosives*, Royal Society of Chemistry, Cambridge **1998**.
[6] B. Holm, *German Patent DE 3 224 477*, **1983**.
[7] R. Matyáš, in *New Trends Res. Energ. Mater., Proc. Semin. 8th* (Ed: J. Vagenknecht), University of Pardubice, Pardubice, Czech Republic, **2005**, p. 2/687.
[8] A. Reichel, O. Roos, J. Wittur, *German Patent DE 2 308 430*, **1974**.
[9] D. C. Wagstaff, D. Clive, *UK Patent GB 2 374 867*, **2002**.
[10] a) B. P. Enoksson, Nitro Nobel AB, *German Patent DE 1 808 922*, **1969**. b) B. P. Enoksson, Nitro Nobel AB, *German Patent DE 19 690 619*, **1969**.
[11] P. J. Langley, J. Hulliger, *Chem. Soc. Rev.* **1999**, 28, 279.
[12] H. S. Kim, S. M. Lee, K. Ha, C. Jung, Y.-J. Lee, Y. S. Chun, D. Kim, B. K. Rhee, K. B. Yoon, *J. Am. Chem. Soc.* **2004**, 126, 673.
[13] G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem. Int. Ed.* **2003**, 42, 3732.
[14] a) F. L. Cozenens, H. Garcia, J. C. Scaiano, *J. Am. Chem. Soc.* **1993**, 115, 11 134. b) C. J. Rhodes, I. D. Reid, E. Roduner, *J. Chem. Soc., Chem. Commun.* **1993**, 512. c) A. D. Trifunac, *J. Phys. Chem.* **1990**, 94, 4751.
[15] S. R. Dunne, *US Patent US 6 251 200 B1*, **2001**.
[16] W. C. Fleming, H. J. McSpadden, D. E. Olander, *US Patent Appl. 753 521*, **1996**.
[17] N. V. Latypov, J. Bergman, *Tetrahedron* **1998**, 54, 11 525.
[18] A. Gindulytė, L. Massa, L. Huang, J. Karle, *J. Phys. Chem.* **1999**, 103, 11 045.
[19] S. M. Peiris, C. P. Wong, F. J. Zerilli, *J. Phys. Chem.* **2004**, 120, 8060.
[20] J. Evers, T. M. Klapötke, P. Mayer, G. Oehlinger, J. Welch, *Inorg. Chem.* **2006**, 45, 4996.
[21] D. C. Sorescu, J. A. Boatz, D. L. Thompson, *J. Phys. Chem. B* **2003**, 107, 8953.
[22] D. C. Sorescu, J. A. Boatz, D. L. Thompson, *J. Phys. Chem. B* **2005**, 109, 1451.
[23] B. Mihailova, S. Mintova, K. Karaghiosoff, T. Metzger, T. Bein, *J. Phys. Chem. B* **2005**, 109, 17 060.
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