High-density storage of H_2 in microporous crystalline silica at ambient conditions

0.6 nm (15 kgm^{-3})

High-Density Storage of H_2 in Microporous Crystalline Silica at Ambient Conditions

Annemieke W. C. van den Berg,[a] Paolo P. Pescarmona,[a] Joop Schoonman,[b] and Jacobus C. Jansen*[a]

Dedicated to Professor Jacob Moulijn on the occasion of his 65th birthday

Abstract: Molecular hydrogen was encapsulated in the cages of clathrasil decadodecasil 3R (DD3R) during the hydrothermal synthesis of this microporous silicate. The crystalline structure of DD3R facilitates high-density hydrogen storage at ambient conditions. Prompt gamma activation analysis (PGAA) revealed that on average about one molecule of H_2 is trapped in each (5^{12}) cage of DD3R. The presence of molecular hydrogen inside the DD3R framework was confirmed by solid-state ^1H NMR spectroscopy. Temperature-programmed decomposition (TPD) in combination with mass spectrometry showed that the encapsulated hydrogen is released upon decomposition of the clathrasil structure. This release can be promoted by the presence of water.

Keywords: clathrates · encapsulation · hydrogen · silicates · zeolites

Introduction

The safe and efficient storage of hydrogen is a necessary condition to be met before hydrogen may be used as a sustainable energy source in replacement of traditional fossil fuels.[1] Still, hydrogen is a very difficult molecule to store. At ambient conditions, H_2 is an explosive gas with a density of 0.09 kgm^{-3}, corresponding to an average nearest neighbour distance of 3.3 nm. Therefore, storage of hydrogen gas requires a high pressure (300–800 bar) in order to reach a reasonable volume capacity. Storage of the much denser liquid (71 kgm^{-3}, 0.36 nm) and solid states is only possible at very low temperatures, 20 and 14 K, respectively. Since such extreme conditions are both dangerous and energetically unfavourable, many alternative H_2 storage methods have been investigated during the last decades.[1,2] The ideal method would allow safe and compact storage at ambient conditions with a minimal energy loss. The stored hydrogen should be readily available for use through a fast and controllable release process.

Microporous solids like zeolites and metal–organic frameworks are characterised by high surface areas and by three-dimensional networks of cages and channels. These features make them interesting candidates for hydrogen storage.[3,5,6] However, the best loadings of H_2 obtained so far with these microporous materials are still below the targets for application and require adsorption at very low temperature (77 K).[3,4,6] Recently, a promising new system for hydrogen storage based on the formation of a clathrate hydrate was reported.[7,8] Clathrate hydrates are crystalline inclusion compounds in which guest molecules occupy cavities made up of hydrogen-bonded water molecules. This system can attain a good loading of hydrogen, but its synthesis requires extremely high pressures (2000–3000 bar). The hydrogen hydrates can be stabilised at lower, but still high pressure (50 bar) by a guest organic molecule.[7]

Here, we present a fundamental study of the storage of H_2 in clathrasils, a family of crystalline microporous silicates related to zeolites, which possess the same framework type as clathrate hydrates.[9] The aim of this work is to investigate the storage capacity of microporous silicates at ambient conditions, which is the ideal state for application of hydrogen as energy source.

[a] Dr. A. W. C. van den Berg, Dr. P. P. Pescarmona, Prof. J. C. Jansen
Ceramic Membrane Centre "The Pore"
DelftChemTech, Delft University of Technology
Julianalaan 136, 2628 BL Delft (The Netherlands)
Fax:(+31) 152-784-289
E-mail: J.C.Jansen@tudelft.nl

[b] Prof. J. Schoonman
Delft Institute for Sustainable Energy
DelftChemTech, Delft University of Technology
Julianalaan 136, 2628 BL Delft (The Netherlands)

Results and Discussion

The formation paths of clathrasils and of clathrate hydrates are very different, though the resulting crystal frameworks are very similar. Clathrates are obtained from a phase transition process, while clathrasils are generally synthesised by hydrolytic condensation reactions in the presence of a help gas (e.g., N_2, CO_2, CH_4), which might get trapped inside the porous structure.[9,10] To study the encapsulation of hydrogen in microporous structures, clathrasil decadodecasil 3R (DD3R) was synthesised in the presence of 50 bar of H_2. Decadodecasil 3R has a DDR framework type (Figure 1),[11]
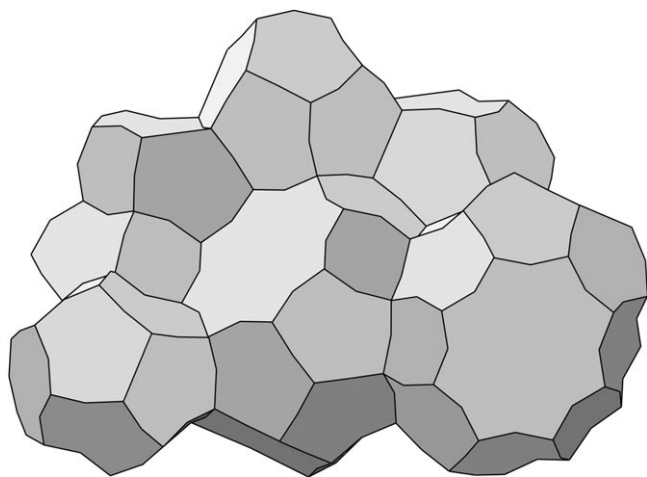

Figure 1. Schematic representation of the cages of DD3R. The silicon atoms are located at the cross-sections where three or four lines join. They are connected by an oxygen atom placed between them. DD3R can be described as $(4^3 5^{12} 6^1 8^3)^2 (5^{12})^3 (4^3 5^6 6^1)^2$: two large $(4^3 5^{12} 6^1 8^3)$ cages, three intermediate (5^{12}) cages and two small $(4^3 5^6 6^1)$ cages.

which presents a certain similarity to the structure of sII clathrate hydrate,[7] since both solids contain (5^{12}) cages, consisting of twelve five-rings (i.e., each containing 5 SiO units). The presence of this type of cage is very important for the purpose of trapping H_2: previous computer simulations showed that clathrasil rings containing six and more SiO units are permeable to hydrogen.[12,13] Therefore, H_2 can relatively easily escape from the $(4^3 5^{12} 6^1 8^3)$ cage through the six- and eight-rings. Although $(4^3 5^6 6^1)$ cages contain a six-ring, this ring is placed between two such cages (Figure 1), a disposition that does not allow escape of the encapsulated hydrogen. Nevertheless, the available volume of this type of cage is expected to be too small to host a hydrogen molecule: the synthesis of clathrasil sigma-2 under very similar conditions to those used to prepare DD3R did not result in trapping of H_2 in the $(4^3 5^6)$ cages, which have a volume comparable to that of the $(4^3 5^6 6^1)$ cages. In agreement with this result, theoretical grand canonical Monte Carlo simulations at 453 K and 50 bar indicate that H_2 is present in the (5^{12}) and $(4^3 5^{12} 6^1 8^3)$ cages, but not in the $(4^3 5^6 6^1)$ cages of DD3R. Therefore, only the (5^{12}) cages in DD3R are considered to be suitable to trap H_2 molecules.

The preferential encapsulation of H_2 compared to H_2O, which has a similar size to H_2 and is present in larger amounts during the synthesis of DD3R, can be explained by the hydrophobicity of the all-silica microporous material.

The synthesis of DD3R requires an organic template molecule, 1-aminoadamantane, which is trapped in the largest cage $(4^3 5^{12} 6^1 8^3)$ during the formation of the clathrasil. In contrast to the case of the clathrate hydrate, the template can easily be removed after the synthesis without affecting the framework. Furthermore, DD3R is stable at ambient conditions.

The clathrasil crystals were prepared by hydrothermal synthesis over two weeks at 453 K, in the presence of 50 bar of gaseous hydrogen. The formation of a pure DD3R phase was confirmed by powder X-ray diffraction (XRD). The XRD-pattern showed no deviations from a pure sample synthesised without H_2. The crystal size distribution of 1–20 μm (Figure 2), as determined by means of scanning electron microscopy (SEM), is caused by sequential nucleation occurring during the reactor heat-up period of two hours.
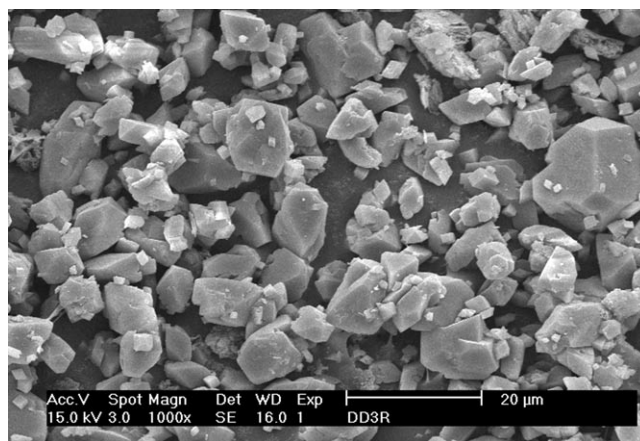

Figure 2. SEM micrograph of DD3R crystals synthesised in the presence of 50 bars of H_2.

The amount of H_2 trapped in the cages of DD3R was determined by means of prompt gamma activation analysis (PGAA). This technique provided the elemental composition of the as-synthesised crystals. An atomic Si/H ratio of $0.964 \pm 1.85\%$ was found. The Si/O and Si/C ratios are in agreement with a loading of one 1-aminoadamantane molecule per $(4^3 5^{12} 6^1 8^3)$ cage. Subtracting the hydrogen contribution of the 1-aminoadamantane gives a ratio of 22.5 hydrogen atoms per 120 silicon atoms. This amount of hydrogen is due to the trapped gas, but also to other sources of hydrogen atoms like hydroxyl groups and water. To estimate the fraction of H atoms not due to H_2, the Si/H ratio was measured for a clathrasil without encapsulated H_2, giving an excess of eight hydrogen atoms for each 120 silicon atoms. This number is in good agreement with calorimetric measurements (vide infra). Subtracting this value and assuming that the remaining H atoms belong to H_2 molecules con-

fined into (5^{12}) cages, an average loading of 0.8 ± 0.1 H_2 molecules per (5^{12}) cage in DD3R is obtained. This value is in the same range as the loading found for hydrogen storage in clathrate hydrates.[7]

The presence of molecular hydrogen in the DD3R crystals was confirmed by means of solid-state proton magic angle spinning NMR (^{1}H MAS NMR) spectroscopy. The spectrum of the as-synthesised DD3R sample shows two main lines (Figure 3a). The broad peak with a chemical shift of $\delta =$
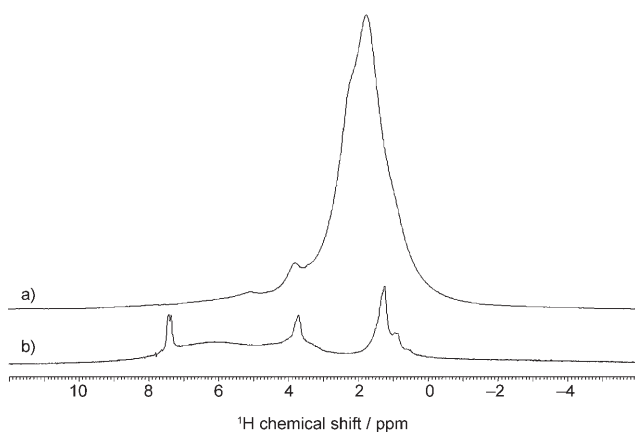
Figure 3. ^{1}H MAS NMR spectrum of DD3R synthesised in the presence of 50 bar H_2, a) prior to and b) after calcination.

Figure 4. Release of H_2, H_2O, N_2, CO and CO_2 (measured by TPD-MS) as a function of temperature for DD3R a) as-synthesised in the presence of 50 bar H_2, and b) after calcination.

1.8 ppm is due to the 1-aminoadamantane template.[14] The less intense, partially hidden peak at $\delta = 3.8$ ppm is assigned to H_2 molecules trapped into the (5^{12}) cages of the DD3R framework, in analogy to the chemical shift reported for H_2 encapsulated in the (5^{12}) cages of clathrate hydrates ($\delta = 4.3$ ppm).[7] The signal of trapped H_2 can be visualised more clearly after removing the template from the DD3R sample by calcination at 873 K for 24 h (Figure 3b). The intensity of the peak is not affected by the calcination, indicating that the storage of H_2 into the DD3R framework is stable to thermal treatment up to 873 K. The spectrum recorded after calcination presents a few other lines. The peaks between $\delta = 0.9$ and 1.2 ppm, which were hidden by the template signal in the spectrum of the uncalcined DD3R, are assigned to silanol groups at the external surface or at lattice defects of the DD3R framework.[15,16] The peaks around $\delta = 7.4$ ppm were absent in the spectrum of the as-synthesised sample. Therefore, they are assigned to products of the decomposition of 1-aminoadamantane that did not diffuse out of the ($4^3 5^{12} 6^1 8^3$) cage and reacted with species adsorbed from air after the calcination. The very broad signal centred at $\delta = 6.1$ ppm is due to H_2O adsorbed in the ($4^3 5^{12} 6^1 8^3$) cages of the DD3R framework after calcination (as confirmed by temperature-programmed decomposition MS analysis, see Figure 4b). Adding a drop of H_2O to the calcined sample caused an increase in the broad water signal without affecting the line at $\delta = 3.8$ ppm, in agreement with the assignment of the latter peak to trapped H_2.
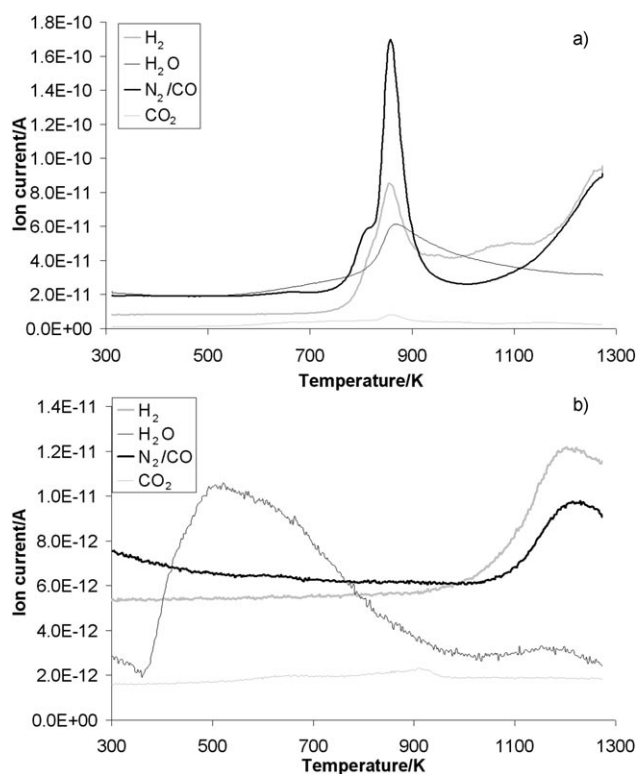
The storage stability of the H_2 molecules in the (5^{12}) cages is very high. This was proven by PGAA measurements of the hydrogen content after storing the DD3R crystals for eighteen months in air at ambient conditions.

It is not trivial to determine how the H_2 molecules are distributed in the (5^{12}) cages. The NMR analysis suggests a homogeneous distribution, but we cannot exclude the possibility that some cages are empty, while others contain two H_2 molecules. To get a better idea of the energy that drives H_2 encapsulation in DD3R, molecular mechanics calculations employing a validated force field[12] were performed. These calculations provided an adsorption energy of 11 kJ mol^{-1} for the first encapsulated H_2 molecule, 9 kJ mol^{-1} for a second H_2 molecule and 5 kJ mol^{-1} for a third one (Figure 5). These values suggest that a single H_2 molecule in each cage is the most favourable situation, although two molecules per cage might occur. Additionally, grand canonical Monte Carlo simulations at 453 K and 50 bar indicate the presence of only one H_2 molecule per (5^{12}) cage, supporting the hypothesis of a homogeneous distribution.

The average distance between the H_2 molecules in the DD3R crystal is only 1.0 nm at ambient conditions, about three times closer than in pure (gaseous) hydrogen at the same conditions. The distance between two H_2 molecules trapped in two adjacent (5^{12}) cages would be as low as 0.6 nm (hydrogen density 14.7 kgm^{-3}), showing the large po-
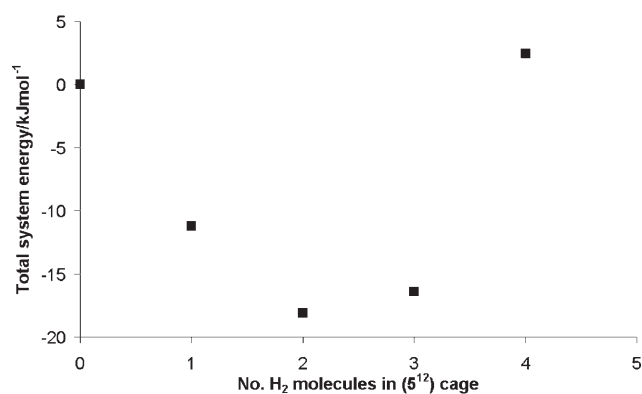
Figure 5. Total system energy relative to the empty DD3R system as a function of the number of H_2 molecules in a single (5^{12}) cage.

Figure 6. Release of H_2 as a function of temperature for the calcined DD3R crystals in a flow of helium with and without 2 vol% H_2O and for silicon carbide in a flow of He with 2 vol% H_2O (measured by TPD-MS).

tential of porous silica for increasing the H_2 density at ambient conditions.

The release of H_2 from the DD3R structure was studied by means of temperature-programmed decomposition (TPD) in combination with mass spectrometry (MS) by using an inert helium flow of 50 STP $cm^3 min^{-1}$ and a heating rate of 10 $K min^{-1}$. This analysis showed that the 1-aminoadamantane can be removed around 850 K, while the H_2 in the (5^{12}) cages is released only above 1100 K (Figure 4a),[17] that is, when the clathrasil structure collapses.[18,19] This result is in agreement with the NMR analysis, which showed that the trapped H_2 is still present after calcination at 873 K. The weight loss after calcination of a fresh sample was 12.1 wt%. As the overall theoretical composition of DD3R is $|(C_{10}H_{17}N)_6(H_2)_9|[Si_{120}O_{240}]$,[10] the expected weight loss due to template removal is 11.2 wt%. The difference is mainly caused by the release of four to five H_2O molecules for each 120 Si atoms. This result is in good agreement with the number of H atoms belonging to SiOH or H_2O that was estimated from the PGAA measurements.

Since H_2 release at temperatures above 1100 K is technically undesirable, we attempted to lower this temperature by adding 2 vol% water vapour to the helium flow. Water can potentially hydrolyse a Si-O-Si bond into two separate Si−OH groups, thereby opening the clathrasil framework, and hence, allowing H_2 to escape at milder conditions. An inert silicon carbide (SiC) sample was used as a blank. The resulting TPD-MS spectra of the H_2 signal are given in Figure 6. The SiC sample showed an exponential increase in the H_2 signal above 1100 K. This is probably caused by thermal decomposition of the water molecules into H_2 and O_2 above this high temperature. This effect also explains the shifted baseline of the H_2 signal for DD3R heated in the presence of water. Comparing the H_2 signals for the DD3R samples shows that adding the water molecules lowers the release temperature by about 50 K. Although this effect is not strong, it does prove the concept that water is beneficial in decreasing the release temperature. Future experiments will establish to which extent this effect can be useful.

In conclusion, high-density H_2 storage in microporous crystalline solids at ambient conditions has been proven for
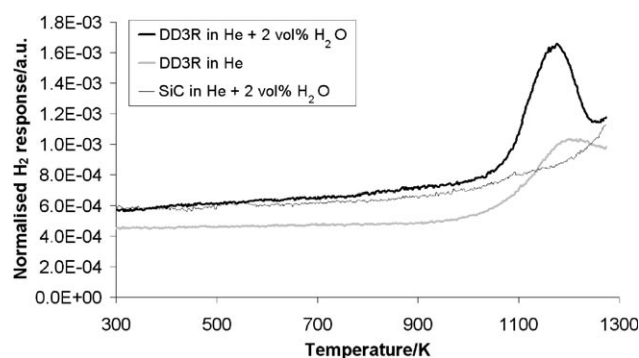
the first time. Conceptually, the results reported here show how the confinement of hydrogen into a porous material can lead to an improved density of storage at ambient conditions by overcoming the repulsion that takes place among the gas molecules. This class of storage materials can be improved by granting an easier release of the trapped hydrogen and a better weight% loading of H_2 than with the clathrasil presented in this work (0.2 wt%). This could be achieved by optimizing a flexible pore aperture function to release hydrogen as well as by increasing the concentration of (5^{12}) cages.

Experimental Section

Synthesis: The molar composition of the reaction mixture used for the synthesis of DD3R is $SiO_2/C_{10}H_{17}N/H_2O = 1.00:0.26:110$. The silica source, tetramethylorthosilicate (TMeOS; Aldrich, 99+%), and the organic template, 1-aminoadamantane ($C_{10}H_{17}N$, Aldrich, 97%), were used as supplied. In a typical synthesis, TMeOS (7.62 g) was added to demineralised water (100 g) in a PE bottle (250 mL) at room temperature ($\pm$ 296 K) and while stirring the water solution at 250 rpm with a magnetic stirrer. The mixture was stirred for 10 minutes and then the stirring rate was lowered to 50 rpm before slowly adding 1-aminoadamantane (2.00 g) with a small spoon. The 1-aminoadamantane has a double function: it is the organic template for the clathrasil and it is a weak base increasing the pH to about 9. The mixture was stirred for one hour at 100 rpm. Alternatively, if the mixture was stirred at 50 rpm until the 1-aminoadamantane was dissolved yielding a white homogeneous suspension (5–6 h), clathrasil sigma-2 (SGT) was obtained instead of DD3R.

After this preparation procedure, the mixture was poured into a Hastelloy-C 200 mL autoclave set-up. The foam, if any, was also transferred to the autoclave. The window of conditions within which DD3R is formed is quite narrow. Adding some DD3R or DOH seeds to the mixture at this stage can help to obtain the desired phase, but is not a necessary condition. Prior to use, all entrance and exit lines of the autoclave were flushed with N_2 to remove the present oxygen. The H_2 entrance lines were subsequently flushed with H_2.

The mixture was stirred at 150 rpm and the air was evacuated from the autoclave by applying a dynamic vacuum for 1 hour at $P < 15$ mbar and room temperature. During this evacuation process the air and the methanol resulting from the hydrolysis of the TMeOS were removed from the autoclave. Next, the autoclave was filled with H_2 up to about 23 bar. The autoclave was gradually heated to 453 K in two hours by means of an electric heating mantle. If the pressure did not yet reach 50 bar at 453 K,

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the H$_2$ inlet was shortly opened again until the desired pressure was reached. This pressure provides an amount of H$_2$ dissolved in H$_2$O that is sufficient to fill all the (5^{12}) cages in an efficient encapsulation of H$_2$ in DD3R. The mixture was kept under these conditions (150 rpm, 50 bar, 453 K) for two weeks. The pressure typically dropped by about 5 bars during this period.

After the synthesis, the autoclave was cooled to room temperature over a period of 30 minutes. The contents of the autoclave were collected and washed three times with demineralised water. The resulting white powder was dried overnight at 393 K (typical yield: 2.5 g = 75 %).

The calcination of the clathrasils was performed in static air at 873 K (heating rate 1 K min^{-1}) for 24 h. The total mass loss after calcination was on average 12 wt %.

Characterisation: The nature of the crystals was determined by powder X-ray diffraction (XRD). The measurements were performed on a Bruker-AXS D5005 diffractometer equipped with a Huber incident-beam Cu$_{K\alpha1}$ monochromator and a Braun position sensitive detector. The 2θ range was 10–70° and the step size was 0.039° 2θ. The specimen was a thin layer of sample material with a weight between 10 and 20 mg, deposited on a Si $\langle 510 \rangle$ wafer as a "zero background" substrate.

The morphologies and elemental compositions of the crystals were analysed with scanning electron microscopy (SEM) on a Philips XL30 FEG SEM that included the possibility for X-ray micro-elemental analysis (Noran Vantage system with a "Pioneer" lithium-drifted silicon detector).

The presence of encapsulated H$_2$ was investigated by means of solid-state ^{1}H MAS NMR spectroscopy. The spectra were recorded on a Bruker AMX300 spectrometer (7.0 T) at the Centre for Surface Chemistry and Catalysis of the University of Leuven (K.U. Leuven; Belgium). The samples were packed in 4 mm Zirconia rotors. 32 scans were accumulated with a recycle delay of 10 s. The spinning frequency of the rotor was 6000 Hz. The spectra were recorded with a single-pulse method. Tetramethylsilane was used as shift reference.

The ratio between the Si, H, N and O atoms was determined by means of Prompt gamma activation analysis (PGAA) by using the facilities of the Budapest Neutron Centre in Hungary.

Finally, the DD3R crystals were analysed with a combination of temperature programmed decomposition (TPD) and mass spectrometry (MS). The measurements were performed in a conventional flow apparatus using a quartz microreactor and He as carrier gas, flowing at 50 STP cm^3 min^{-1}. About 0.1 mg of sample was heated up to 1273 K with a rate of 10 K min^{-1}. The desorption processes of gaseous species from the sample were monitored by a quadrupole mass spectrometer (Balzers QMS200) connected on-line with the reactor. Mass spectra were recorded in a multiple ion detection (MID) mode by using a channeltron detector. The released gases with a number of predefined molecular weights (H$_2$: 2 g mol^{-1}, H$_2$O: 18 g mol^{-1}, N$_2$/CO: 28 g mol^{-1}, O$_2$: 32 g mol^{-1}, CO$_2$: 44 g mol^{-1}) were continuously monitored during heating.

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