Scientific Report

on the implementation of the project **PN-II-IDEI 305/2011**

during the stage October-December 2011

The theme of the project:

The surface effect on the dynamics of molecules confined inside porous media with magnetic impurities

The objective of the stage 2014:

Preparation and the characterization of porous media with a controlled amount of magnetic impurities

The associated activities:

A1. Preparation of porous samples with different amounts of magnetic impurities;

A2. Characterisation of the produced samples with respect to the magnetic susceptibility;

A3. Characterisation of the produced samples with respect to the porosity and the pore size distribution.

Introduction

Nuclear magnetic resonance (NMR) is one of the most advanced techniques for investigating the dynamics of molecules confined inside porous media. The NMR diffusometry and relaxometry studies allow obtaining of information about the interactions of molecules with the walls and the structure of porous media (pore size, porosity, tortuosity) [1,2]. These data are generally obtained by two types of measurements: the NMR difuzometry [1] and the NMR relaxometry [2]. Natural porous media (rocks, concrete, soils) may however contain magnetic impurities which can decisively influence the interpretation of experimental results or even make impossible the NMR experiments at all [3]. Therefore, understanding the role of magnetic impurities and of the internal gradients in NMR experiments [4] is vital for performing accurate measurements and is one of the objectives of this project.

Natural porous media may have uncontrollable amounts of magnetic impurities heterogeneously distributed inside their structure. Therefore, the theoretical models developed to explain the experimental results often fail or are generally limited to a particular sample or a specific experiment [4]. To refine the NMR methodology is therefore necessary to create model samples with a controlled amount of magnetic impurities allowing a correct interpretation of the experimental results and the role of molecules interaction with the surface on molecular dynamics. The objective of the stage 2011 was the creation of such samples and their characterization in terms of their structural and magnetic properties. These samples will be used in subsequent stages of the project as templates in the investigation of molecular dynamics at the interface.

1. Preparation of porous ceramic with a controlled amount of magnetic impurities

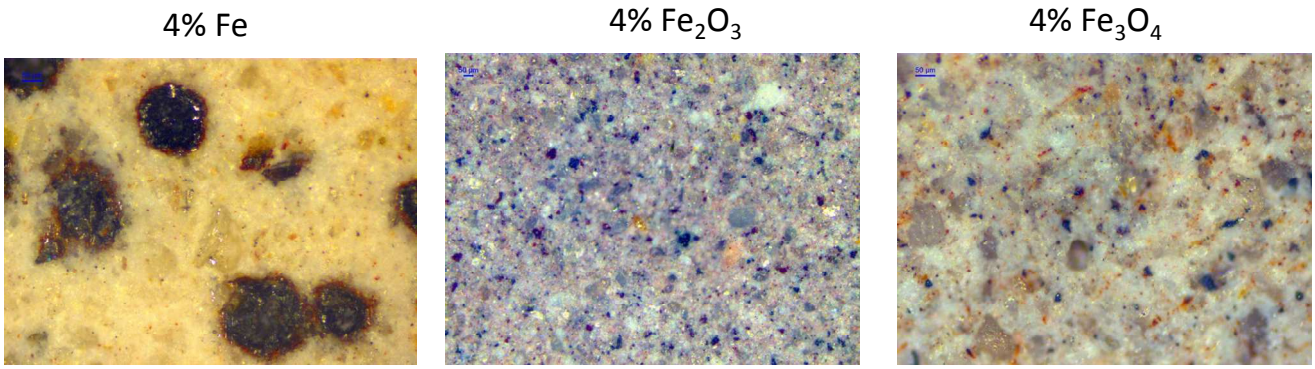

Fig.1. The optical images of the produced samples for the same quantity of magnetic impurities but of a different nature. One can observe the formation of ferromagnetic clusters in the case of samples containing Fe and the absence of the NMR signal of the confined molecules inside these samples. Therefore only the samples containing Fe_2O_3 and Fe_3O_4 as magnetic impurities will be used in our future investigations.

Among the many possibilities of obtaining porous media with a controlled amount of magnetic impurities in this stage we have chosen the manufacturing of porous ceramics [5]. They are easy to produce and have many industrial applications which justify the study of surface effects on molecular dynamics of molecules confined inside these porous media. In recent years several new methods of producing such materials were developed, aiming in particular ceramic composition, change internal network and mechanical properties, thermal, electrical, optical or corrosion resistance. Depending on the properties required for a particular application the experimental conditions for the production of porous materials changes [5-7].

One of the oldest methods of producing porous ceramic materials is based on the pressed powder. Here the shape and the size of pores is determined by the size distribution of the raw materials, their shape, their chemical composition and the thermal treatments to which the mixture is subjected to [7]. This method of production was chosen to be used in our project after we have previously investigated the possibility of using a polymeric sponge method which proved to be less effective. The raw materials used in the preparation were kaolin, sand and feldspar. The introduction of magnetic impurities was made in a controled way by using the raw materials which have properties that are present in many natural porous media. The materials selected by us were: Fe_3O_4, α-Fe_2O_3 and the metallic iron. Note that both kaolin and feldspar sand may contain magnetic impurities which will influence the amount of impurity that is intended to be introduced. Kaolin, in its natural state, always contains trivalent iron impurities (mainly due to its possibility to replace aluminum, also trivalent), but in a very low percentage. In sand instead the iron impurities can have considerable percentage, so sand was used for sample preparation with known chemical composition or sand has previously been deferrized.

The main features that are targeted at a powder are: particle size distribution, particle shape, the degree of agglomeration, the chemical composition and purity. For the synthesis of ceramic powders there are several methods, of which the most common are milling, grain size reduction by chemical methods involving chemical reactions under strict parameter conditions. Insufficient knowledge of the chemical composition or purity of the powder can lead to unwanted defects in the final microstructure of the material [7]. Decreased constituent particle size showed large increases in efficiency and quality of the final product, but their control comes with a disadvantage: if the particles have sizes below 1µm they have a high tendency for agglomeration, leading to inomogenities in the properties at different positions in the sample [7]. Pressing of the raw materail requires semi-dry shaping by adding water or ethanol and thus providing the necessary mass plasticity of the sample so that after pressing it mainains the shape before firing it. In most cases the microstructure before firing controls the microstructure of the final product because the processes occurring during firing are unable to "correct" the environmental homogeneity defects the grain size introduces and even the clusters formed [7].

The methodology used for the preparation of our samples is described below. The composition of the powder in mass ratio contains: 60% kaolin, 10% sand, 30% feldspar. To each 100g of this mix was added 2, 4, 6, 8 and

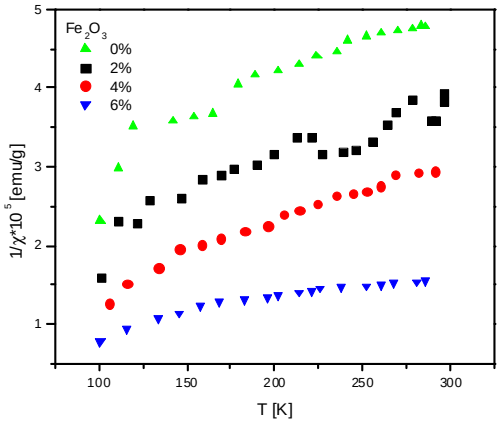

Fig.2. The dependence of the inverse susceptibility versus temperature for 4 samples containing Fe_2O_3.

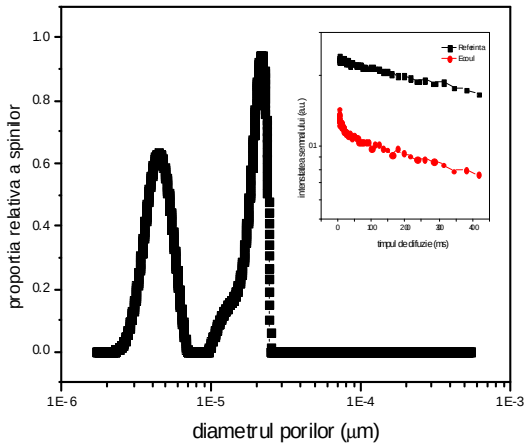

Fig.3. The pore size distribution of the porous ceramics containing 2% Fe_2O_3 extracted via the DDIF technique. The inset shows the two signals recorded in a DDIF experiment.

10 g of metallic iron, Fe_2O_3 or Fe_3O_4, respectively. The raw materials were purchased from Alfa Aesar company that offered also the oxide composition. The raw materials used were sieved to the desired particle size by using 0,080mm and 0.125mm sieves. Two different granulometries were considered for each type of magnetic impurity added. The obtained samples are porous cylinders of 7mm height and 8mm diameter to be placed in the NMR tube. We also prepared two samples without magnetic impurities for each sample set. The reason for choosing the two different particle size distributions was to get a different porosity for each sample with magnetic impurities (metallic iron, Fe2O3, Fe3O4). The thermal treatment of the manufactured samples consisted of keeping them in an electric oven at 1150 ^{O}C for 1h followed by a slow cool down for 24h. From the point of view of the mechanical properties of the samples as well as the X-ray diffraction they confirmed the formation of the crystalline lattice. In Figure 1 are shows the optical images for 3 of 36 samples. The images recorded with a Leica microscope DM2500M.

A2. Characterisation of the produced samples with respect to the magnetic susceptibility;

In order to characterize the samples containing a variable amount of magnetic impurities from the point of view of the magnetization the susceptibility constant of some of these samples has been measured in the temperature range between 80 and 300K. The experimental determination has been done using a standard Faraday magnetic balance [8]. The experimental results on samples containing of Fe_2O_3 magnetic impurities are shown in Figure 2 for several concentrations of impurities. One could notice a linear increase of the paramagnetic component of sample magnetization with the magnetic impurity content. The same results could be indirectly probed by NMR relaxometry measurements and EPR measurements. This information will be used in the subsequent NMR experiments.

A3. Characterisation of the produced samples with respect to the porosity and the pore size distribution

The produced samples were characterized in terms of the porosity and the pore size. We refer here only to interconnected pores because only they can be saturated with liquid and are of interest for studying molecular dynamics. The porosity of the manufactured samples was determined both by gravimetric measurements and from NMR signal strength. The measurements have indicated for the produced samples porosities between 17 and 25%.

The information about the pores size could be extracted from optical microscopy combined with image analysis techniques (using ImageJ software). The samples showed a bi-modal distribution in pore sizes over a range 1-7μm and 10-50μm, respectively. The smaller size of the pores was observed in the samples using two different sizes of kaolin particles in the preparation, even if the pressure was lower. This information will be very important in the interpretation of experimental NMR data to be obtained in subsequent stages of the project and for preparing new samples. To obtain the pore size distribution, a very useful technique proved to be the diffusion decay in the

presence of internal gradients technique (DDIF - Decay due to Diffusion in Internal Field) [9, 10]. The results obtained with this technique also confirm a bi-modal distribution of pore sizes.

Conclusions

In this stage we have investigated the possibility of producing porous ceramics with increased amount of magnetic impurities. For the magnetic characterization of the samples the magnetic susceptibility measurements, electron spin resonance and NMR relaxometry was used. The porosity of the produced samples was extracted from gravimetric measurements and NMR measurements. The pore size distribution was obtained using the DDIF technique which has been applied for the first time in the world for systems containing magnetic impurities introduced in a controlled way. At present an analysis of the possibilities and limitations of this technique is done and a scientific paper to be submitted for publication to Journal of Magnetic Resonance is in preparation.

References

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