EPR in functional structures based on doped (nano, meso)-porous silica and titanium dioxide

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Abstract. EPR investigations are performed on mesoporous silica (SBA15) functionalized by
Nickel-cyclam complexes (1,4,8,11-tetraazacyclotetradecane groups chelating nickel ions) and
on mesoporous titanium dioxide with nitrogen doping. For functionalized silica, the magnetic
behaviour of organometallic groups, their mutual interactions and dispersion in the host
matrices are compared with respect to the doping rates and the synthesis procedures. The
relaxation processes were analyzed from the thermal evolution of the paramagnetic spin
susceptibilities and EPR line-widths. Particularly, some samples show the formation of clusters
where phonon assisted one dimensional (1D) ferromagnetic ordering occurs below 45 K. For
the mesoporous TiO₂, systematic EPR investigations were performed on two main classes of
materials with regard to the porosity degrees. The EPR experiments point out the efficiency of
EPR method to probe the degree of functionalization of mesoporous silica or the nitrogen
doping achievement in TiO₂, and in general to give a valuable feedback to improve the
synthesis routes of smart materials.

1. Introduction

Nanostructures based on functional mesoporous silica or titanium dioxide are attractive materials for
versatile applications in catalysis [1,2], bio-sensing [3], drug delivery [4, 5], photovoltaic conversion,
CO₂ sequestration or degradation of organic pollutants. Several strategies for the synthesis routes
were developed to obtain the well known SBA-15 mesoporous silica with variable pore size ranging
from 2 nm – 50 nm. Also, nanoparticles or active molecules with original magnetic, optic or charge
transfer properties, can be grafted in the channels or even incorporated in the host matrix backbone
[6]. The high specific surfaces ensure a grafting of a large amount of active groups required for
enhanced physical responses leading to effective applications. However, the main problem
encountered in the functionalization process lies in the formation of aggregates or clusters of the active
groups. In this context, by using paramagnetic organometallic molecules as functional vectors in
mesoporous silica, the EPR technique was successfully applied to probe these active groups including
their local environment, mutual interactions, dispersion in the host matrices and the correct
achievement of the material processing. Analyses of the relaxation mechanisms and thermal behavior
of the spectral EPR parameters were performed to give information on the intrinsic electronic and
magnetic of organometallic groups as well as the degree of functionalization of the silica matrices.

The second class of investigated mesoporous materials is based on TiO2 with or without doping
agents. By using TiOCl₂ as precursor of mesoporous matrix, thiourea for nitrogen doping and P123 as
the structuring agent, TiO₂ powders with different degree of ordering and porosity were synthesized
[7]. The efficiency of doping and the determination of the electronic features consecutive to the
presence of doping agents were investigated by EPR technique. Different paramagnetic species mainly
due to oxygen radicals were revealed with the nature and stability dependant on the calcinations
temperature up to 500°C. The nitrogen based radicals were identified and their molecular structure and stability are discussed with regard to the sample features from the synthesis and treatment conditions.

2. Experimental

2.1. EPR spectroscopy
EMX Bruker spectrometer, equipped by X-band, was used with variable temperature equipment using an Oxford Instrument cryostat which allows a temperature stabilisation within ± 0.02K from room temperature down to 4 K. Due to the high concentration of paramagnetic species, low micro-wave power (< 2 mW) and low modulation field (< 0.5 Gs) were typically used to record the EPR spectra far from saturation conditions.

2.2. Mesoporous materials

2.2.1. Functionalized silica matrices
Two families of mesoporous silica functionalized by Nickel-cyclam molecules were synthesized according to the process described in references [6]. The sample features is depicted briefly in figure 1 with the main steps such as the realization of mesoporous silica backbones and the grafting of the Nickel-cyclam molecules inside the pores.

![Figure 1. Mesoporous silica with the functionalization of the pores by metal-cyclam groups.](image)

Two synthesis procedures, namely A and B, were developed to obtain the functional materials. The main differences lie in the dispersion of active groups (Ni-cyclam) in the host matrices and then different magnetic behaviors are expected for the nickel based molecules. Particularly, the procedure (A) give rise to non- homogeneous grafting while procedure (B) allows obtaining homogeneous distribution of active groups inside the pores. The investigated samples are hereafter referenced as (SA5) from procedure (A) and (SB2, SB5, SB11) from the procedure B. The doping rates by Ni-cyclam are (2%) in SB2 sample, 5% in SA5 and SB5 samples, and 11% in SB11.

2.2.2. TiO₂ based materials
The investigations were carried out on two families of titanium dioxide materials synthesized by sol-gel method. One class is dedicated to mesoporous network (or structured) by using P123 as surfactant
and the second one without any porosity is referenced below as non-structured materials. For all samples, the nitrogen incorporation in the TiO$_2$ network was from thiourea. For the main relevant details on the sample, we may below summarize briefly the material features.

**Structured and nitrogen doped mesoporous TiO$_2$**. The synthesis of structured samples is based on mixing in ethanol solution, the precursor of TiO$_2$ such as titanium oxychloride, P123 as surfactant and thiourea for nitrogen doping. The formation of gel followed by a calcination at several temperature and time durations lead to powders samples with crystalline phases of TiO$_2$ mainly such as anatase and rutile with the nomenclature SN-TiO$_2$-400-0.5, SN-TiO$_2$-400-4.5 and SN-TiO$_2$-500-12. The first letter “S” denotes that we deals with structured TiO$_2$, the second letter “N” is related to Nitrogen doping and the rest standing for the treatment temperature and time (h).

**Non-structured and doped mesoporous TiO$_2$**. Similar synthesis procedures were performed to obtain TiO$_2$ without any porosity. In this aim, no P123 surfactant was required and titanium tetraisopropoxide was used as the titanium dioxide precursor. All reactants were dissolved in ethanol which is removed under reduced pressure lading then to the formation of a gel. Calcination of the products was performed at 400°C and 500°C to obtain the samples in the same conditions as for the structured ones. These non-structured samples will be designated hereafter by the following nomenclature N-TiO$_2$-400-0.5, N-TiO$_2$-400-4.5 and N-TiO$_2$-500-12.

Comparative X-ray diffraction investigations were performed on same representative samples. Structured doped or undoped samples exhibit different crystalline orders even under the same calcination conditions [7]. Thus, undoped samples show a coexistence of crystalline polytypes for a short time duration (0.5 h) of calcination at 400°C. At the opposite, nitrogen doped samples under the same treatment conditions reveal only one polytype (anatase) and the superposition of polytypes occurs only for longer time of calcinations (4.5 h). The behavior of the non-structured TiO$_2$ is also quite different and even for long time of calcinations (4.5 h), only rutile-like order is realized in the sample with only anecdotic anatase content. Also, what can be addressed from such analysis are the different crystalline orders involved in the samples after similar treatments.

Representative samples of the investigated series were annealed at 500°C and their structural features were compared. Thus, the structured or non-structured samples which were treated at 500°C overnight are pure anatase despite doping or structuring. Thus, calcination at 500°C during 12 h was adequate to produce pure anatase out of the various preparations. It should be noted here that during this treatment, the mesostructure is completely destroyed [7].

### 3. EPR investigations: experiments and discussion

#### 3.1. Mesoporous silica functionalized by Nickel-cyclam

**3.1.1. Representative Sample from synthesis procedure A**

CW-EPR spectroscopy is used to characterize the effective achievement of the sample synthesis and its correct functionalization by the active groups. Figure 2 reports the thermal evolution of EPR spectra recorded on the sample (SA5) in the temperature range [200K, 5K]. A single EPR line is clearly shown below 200 K and its intensity increases when the temperature is varied from 200 K to 60 K. Additionally, a net narrowing of the line width is observed down to 60 K. At lower temperatures, the intensity loss and the development of broad features are indicative of magnetic ordering which will be discussed below.

The EPR signal of nickel ions in the SA5 sample, consists in a single and symmetric line located at the effective g-factor = 2.20(3) at 100 K. This value correspond to nickel ions in the valence state Ni$^{3+}$, with an effective spin $S = 1/2$ and the electronic configuration $^2\text{E}_g$ as a ground state. The absence of anisotropy, hyperfine or superhyperfine couplings with nearest ligands such as chlorine or nitrogen ions, suggests the formation of Ni-cyclam clusters in the SA5 sample.
Figure 2. Thermal behavior of EPR spectra [8] in the sample (SA5) obtained by the procedure (A) (see the text) and containing a rate of doping about 5% by Nickel-cyclam groups.

The thermal evolution of the EPR spectra of SA5 sample brings the mark of the relaxation phenomena and the interaction between paramagnetic species. The results concerning the line intensity and line width are summarized in figure 3. The thermal evolution of the EPR line intensity was fitted according to the Curie-Weiss law \( \chi(T) = \frac{C}{T - \theta} \). The parameter \( \theta = 38K \) indicates that ferromagnetic exchange interactions hold between spins which can be also represented by a magnetic exchange integral \( J \) through the relation \( \frac{J}{k_B} = -\frac{38K}{2zS(S+1)} \approx -38K \). \( S = 1/2 \) refers to Ni\(^{3+}\) ion and \( z \) represents the number of interacting ions which was fixed at \( z = 2 \) with regard to the expected molecular arrangements.

Figure 3. Thermal evolution of the EPR spectrum line intensity (a) and line width (b).

In the temperature range [200 K, 60 K], a monotonous decrease of the line width (\( \Delta H \)) with the temperature is observed. Below a temperature around 45 K, a divergence of the line width is supported by the occurrence of magnetic transition. Indeed, a magnetic ordering, ferromagnetic or anti-ferromagnetic seems involved in the Ni-Cyclam based clusters and induces a divergence of the correlation length of spin-spin interactions at the critical temperature \( T_c \approx 45K \). The fitting curve of the EPR line width requires two main terms. One is related to a critical contribution behind the line
width divergence due to a magnetic ordering and the other from dynamic Jahn-Teller effect mediated by the spin-spin exchange interaction according to the following expression [8, 9]:

$$\Delta H(T) = A(T - T_c)^\nu + B \exp(-\Delta/k_BT)$$

The obtained fitting parameters are:

$$A(Gauss) = 920, \quad T_c = 45 K, \quad \nu = 0.5, \quad B(Gauss) = 2040 \quad and \quad \tilde{\Delta} = 315 K$$

The energy barrier $\tilde{\Delta}$, in the order of 220 cm$^{-1}$, makes us confident in the correct assignment of the relaxation process as monitored by Jahn-Teller effect on the Ni$^{3+}$ ions. However, the amplitude B $\sim 10^{10}$ s$^{-1}$ cannot discriminate clearly between the phonon-controlled tunnelling or the Orbach-Aminov relaxation phenomena [10]. The relaxation mechanisms are monitored by the dynamic Jahn-Teller effect at high temperature mediated by the exchange interactions between Ni$^{3+}$ ions. Cooperative phenomena seems involved and lead to a magnetic transition below 45K with the features of ferromagnetic-like order.

3.1.2. EPR in representative samples from synthesis procedure B

The EPR spectra recorded at 100K are summarized in figure 4 for SB 2,5,11 samples. At a first glance, the doping ratio is directly traduced on the central and well resolved EPR signal around $g = 2.18$. The existence of a superhyperfine structure on the EPR spectra indicates the dispersion of Nickel-cyclam groups inside the silica pore with the molecule conformation depicted in figure 5d. The broad resonance absorption background observed in the low magnetic field range is a consequence of the existence of agglomerated groups. From the thermal evolution of the EPR spectra, no critical behaviour was observed on the line intensity, line width or line positions. The isolated Ni-cyclam groups involved in the samples from the procedure (B) didn’t show any critical behaviour or magnetic interactions.

![Figure 4](image.png)

**Figure 4.** EPR spectra [8] from the samples synthesized by the procedure (B). (a) comparative spectra with different doping rates by nickel-cyclam, (b) magnification of the central part of spectra to resolve a superhyperfine structure, (c) thermal evolution of central part of the spectra and d) the nickel-cyclam molecule.

3.2. Mesoporous titanium dioxide
The performed EPR investigations compare the paramagnetic centres (PC) signatures in the structured and non-structured N-TiO$_2$ powders. The expected effect is related to changes on the electronic and optical properties of the host matrix. In the synthesized samples, examples of the EPR spectra are shown in figures 5 for the structured sample (figure 5a) and the non-structured ones (figure 5b). As a main PC in the structured samples, O$_3^-$ radicals or alternatively F centres give rise to the characteristic axially symmetric g-tensor whose components are ($g_\perp = 2.004$, $g_\parallel = 2.007$). The discrimination between these centres is not so easy with regard to previous reports in TiO$_2$. However, the evolution of the EPR signal with the calcination of the sample at high temperature suggests the relevance of O$_3^-$ radicals. On other hand, no EPR signal was identified as resulting from nitrogen based radicals. This possibility is realized only when the samples are annealed at 500°C during 12 h. In the structured sample, the development of an important EPR signal characteristic of NO radicals occurs in detriment of PC such as O$_3^-$ species. The tendency of nitrogen to be associated to Oxygen and the disappearance of O$_3^-$ suggest the occurrence of NO radicals on the surfaces of voids or pores in the TiO$_2$ host matrix. The nature of the stabilized NO centres indicate that oxygen molecules can be evacuated from the mesoporous structure after calcination at high temperature (500°C).

**Figure 5.** EPR spectra recorded on the structured samples (a), non-structured samples (b) at different calcinations temperatures and time durations. In figure (c) the labels a,d designate the simulated spectra for samples calcinated at 500°C by using spectral parameters related to nitrogen $N^*$ and NO$^-$ radicals as explained in the text.

**Table 1.** Spectral EPR parameters in the nitrogen doped structured and non-structured samples submitted to calcinations at 500°C.

|        | $g_1$ | $g_2$ | $g_3$ | $A_1$ ($10^3$ cm$^{-1}$) | $A_2$ ($10^3$ cm$^{-1}$) | $A_3$ ($10^3$ cm$^{-1}$) | $\Delta H_1 = \Delta H_2$ (Gs) | $\Delta H_3$ (Gs) |
|--------|-------|-------|-------|--------------------------|--------------------------|--------------------------|-------------------------------|-------------------|
| Non-structured | 2.003 | 2.003 | 2.001 | 2.3                      | 4.2                      | 30.0                      | 2                            | 3                 |
| Structured    | 2.003 | 2.000 | 1.935 | $-0.0$                   | 30.0                     | 10.0                      | 6                            | 20                |
In the non-structured samples (figure 5b), the EPR investigations show quite different PC with respect to the structured samples. Thus, O$_3^-$ radicals, peroxide radicals O$_2^-$ and Ti$^{3+}$ paramagnetic ions coexist in the non-structured samples annealed at 400°C whatever the time duration (0.5 h, 4.5 h). Nitrogen doping effects is shown in the non-structured samples only when the calcination is performed at 500°C during 12 h [11]. The shape of the EPR spectra, marked by quite narrow lines; points out the good crystalline quality around the nitrogen paramagnetic centres involved in the bulk TiO$_2$. The simulated spectra (figure 5c) was achieved by using $S = \frac{1}{2}$ as electronic spin coupled to nuclear spin I = 1 as expected for paramagnetic centres involved in the vicinity of nitrogen ions. The following parameters deduced from adjustment of the spectra are summarized in the table 1.

4. Conclusion
The performed EPR experiments give valuable information on the organisation of active groups in mesoporous silica or the doping efficiency in mesoporous TiO$_2$. For silica based samples, the magnetic behaviour of nickel-cyclam molecules depends on the synthesis procedure. For the procedure named (A), agglomeration of active groups lead to one dimensional magnetic ordering of nickel-cyclam molecules. In the opposite, isolated nickel-cyclam molecules were clearly obtained by the procedure B. For TiO$_2$ samples, the carried out experiments show the general tendency of the nitrogen doping effect to be efficient only when the calcination is performed at temperature as high as 500°C. The nonstructured samples show the relevance of nitrogen centres being incorporated in the bulk TiO$_2$ while only NO radicals are involved in the structured samples. These results point out the role of the mesostructure (structured network) to stabilize the effective doping agents in the bulk structure.

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