

Nickel(II) and manganese(III) tetraazaannulenes complexes encapsulated in porous Vycor glass (PVG): investigation of catalytic activity

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Abstract

The first immobilization of Ni(II) and Mn(III) metallotetraazaannulene compounds in nanometric pores of an inorganic matrix (porous Vycor glass, PVG) by diffusion of the complex through the glass pores is reported. The immobilization process was monitored by UV–vis spectroscopy at room temperature and electron paramagnetic resonance spectroscopy (EPR) at 77 and 300 K. Results showed that the manganese(III) complex was reduced inside the PVG after the immobilization process. On the other hand, the NiTMTAA (tetramethyl dibenzotetraaza[14]annulene of nickel(II)) remained stable. The catalytic activity of NiTMTAA as model of Factor F₄₃₀ on the reductive dehalogenation of alkyl halides (iodocyclohexane or bromocyclohexane) was studied in homogeneous and heterogeneous systems in the presence of NaBH₄ as reducing agent. The promising catalytic results have shown adequate characteristics of PVG for immobilization of the Ni(II) tetraazaannulene complex. These nanocomposites display high potential for heterogeneous catalytic procedures.

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1. Introduction

Compounds containing the tetramethyl dibenzotetraaza[14]annulene framework, frequently named by TMTAA ({5,7,12,14-tetramethyldibenzo[*b,i*]-1,4,8,11-tetraaza[14]annulene) nickel(II) (Fig. 1a) have attracted attention because they can be conveniently synthesized and because they share common characteristics with metalloporphyrins (both contain a dianionic-conjugated ligand with four nitrogen atoms coordinating to the metal) [1]. However, the framework flexibility and ruffled structure of the TMTAA complex, caused by their smaller conjugation in comparison to porphyrins, allows an easy change of the oxidation state from the central metal ion. This is a key difference between tetraaza and porphyrin complexes, which has increased the interest in the former compound as biomimetic model. The framework flexibility allows the macrocycle to accommodate

different coordination geometries [1–4]. This characteristic can facilitate the reduction of Ni(II) to Ni(I), an important property for idealizing model compounds for biological systems [5,6]. In fact, the dibenzotetraaza[14]annulene complexes of transition metals have been studied as models of different enzymes such as vitamin B₁₂ coenzyme by cobalt tetraaza [3], as a model for cytochrome P-450 in oxidative homogeneous reactions of nitro compounds by manganese tetraaza [1] and as a model for Factor F₄₃₀ in catalytic studies of the reductive dehalogenation of alkyl halides to yield alkane in reactions catalyzed by NiTMTAA [6].

Factor F₄₃₀ is an interesting system to be mimetized by tetraaza complexes. Factor F₄₃₀ is the prosthetic group of methyl-coenzyme M-reductase formed by a nickel-hydrogenated porphyrin (MCR) [7], which catalyzes the final stages of the carbon dioxide reduction to methane in methanogenic bacteria [7–9]. In the final step of catalytic cycle, the reduction of Ni(II) to Ni(I) is observed. Studies of this step have shown that the nickel reduction is possible due to the flexible framework, which easily accommodates

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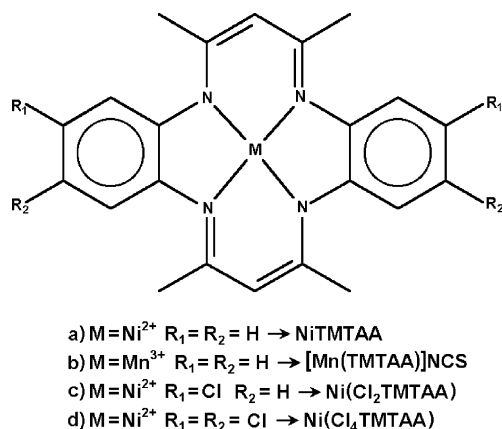


Fig. 1. Molecular structure of {5,7,12,14-tetramethylbenzo[*b,i*]-1,4,8,11-tetraaza[14]annulene}; (a) NiTMTAA; (b) [Mn(TMTAA)]NCS; (c) Ni(Cl₂TMTAA) ({5,7,12,14-tetramethylchlorobenzo[*b,i*]-1,4,8,11-tetraaza[14]annulenate} nickel(II) [27b]) and (d) Ni(Cl₄TMTAA) ({5,7,12,14-tetramethyltetrachlorobenzo[*b,i*]-1,4,8,11-tetraaza[14]annulenate} nickel(II) [27b]).

the N–Ni distances required by the relatively large Ni(I) ion [6,9]. Similar deformation of reduction to Ni(I) has also been observed with synthetic tetraaza complexes whereas the formation of Ni(II) π anion radical in porphyrins leaves the Ni–N distances unaltered [4]. The comparison between these two systems indicates that the flexible framework of the nickel dibenzotetraaza[14]annulene, may facilitate the formation of Ni(I) species [4,6] on the biomimetic reaction.

Inorganic compounds such as silica gel, clays and zeolites have been extensively investigated as matrices for the immobilization of metal complexes [10]. The composites formed can be used as a heterogeneous catalyst in reactions as biomimetic models for a great number of biological systems. Moreover, the matrix structure can provide a better selectivity for the approach of the substrate to the active sites of the immobilized compound [11]. The metal complexes such as macrocyclic complexes have shown important properties for their use as catalysts due to their resistance and flexibility, providing robust catalysts for oxidation and reduction reactions when associated with inorganic supports [12–15]. The immobilization of metallotetraazaannulene combines their properties (resistance and flexibility) with the characteristics associated with the supports such as selectivity and facilitated reuse of the catalysts after the reaction [11].

Porous Vycor glass (PVG) is an inorganic host matrix that can be used to produce several nanocomposites with a great variety of materials, such as semiconductors, oxides and polymers [16–18]. It is a transparent porous material obtained by acid leaching of a phase-separated alkaline borosilicate glass [18]. The PVG shows an open porous structure of essentially pure silica with interconnecting pores ranging between 20 and 200 Å [19], and a pore volume of nearly 28% [16–18]. The porous surface contains slightly acidic silanol groups that can be used as active sites on the incorporation of organometallic, metal complexes and semiconductor compounds [16–18].

Immobilization of porphyrins and metalloporphyrins in porous glasses has been reported in the literature especially in sol–gel derived materials [20–22]. More recently iron and manganese porphyrins were immobilized inside porous Vycor glass and their activity was investigated as catalyst for oxidation reactions [10]. These results suggested that other tetraaza compounds could be immobilized in the porous systems of the PVG. Although the catalytic activity of metallotetraazaannulene was reported in homogeneous catalysis [1,6] heterogeneous catalysis was never reported.

In this paper we report the first immobilization of metallotetraazaannulene compounds (Fig. 1) in nanometric pores of an inorganic matrix (PVG) and the characterization of the solids obtained by EPR and UV–vis spectroscopies. The catalytic activity of NiTMTAA as model of Factor F₄₃₀ on the reductive dehalogenation of alkyl halides on homogeneous and heterogeneous systems was studied.

2. Experimental

All chemicals were purchased from either Aldrich or Sigma and used without further purification, except for the absolute ethanol, methanol and diglyme. These solvents were previously purified [23] and stored under molecular sieves. UV–vis spectra were recorded in an HP 8452A Diode Array Spectrophotometer in the 190–820 nm range. Spectra of the plate samples were obtained by placing the samples directly in the beam path, using air or a PVG plate as reference. The plate surface was positioned perpendicular to the light beam. The dichloromethane solutions of the compounds NiTMTAA and [Mn(TMTAA)]NCS were analyzed in a 1.0 cm path length quartz cuvette and dichloromethane was used as reference. Electron paramagnetic resonance measurements (EPR) of the PVG and the NiT-PVG solids or frozen solutions of the pure nickel complex were performed with a Bruker ESP 300E spectrometer at X-band (ca. 9.5 GHz) at 293 or 77 K using liquid N₂. ¹H NMR measurement was made using Bruker AC80, 80 MHz in CDCl₃ or CCl₄.

2.1. Treatment of the PVG

Code 7930 porous Vycor glass (PVG) was purchased from Corning Glass. Plates of PVG with dimensions of 10 mm × 10 mm × 1 mm in size were first dipped in a 2 mol L⁻¹ HCl solution for 30 min, and then in acetone for another 30 min. After this, the glass plates were heated at 550 °C for 72 h, cooled at room temperature and stored in a desiccator prior to use [24].

2.2. Synthesis

2.2.1. Ni(II)TMTAA

The Ni(II) macrocycle was synthesized following the procedure outlined by Goedken [4]. The NiTMTAA formation was monitored by the UV–vis analysis through the ob-

served changes at 272 and 398 nm [25]. Yield: 60%. UV–vis (CH_2Cl_2) λ_{max} (molar extinction coefficients are given in parentheses, $\text{mol}^{-1} \text{L cm}^{-1}$); 272 nm (30,700), 398 nm (37,700) and 592 nm (6700). Anal. calcd for $\text{C}_{22}\text{H}_{22}\text{N}_4\text{Ni}$ (MM = 401.38 g/mol). C, 70.4%; H, 6.3%; N, 12.7%. Found C, 65.9%; H, 5.6%; N, 13.9%. $^1\text{H NMR}$ (CCl_4); δ 2.1 ppm (12H), δ 4.9 ppm (2H) and δ 6.6 ppm (8H). FT-IR (KBr, cm^{-1}): 3062 (w, =C–H), 3040 (w, C=C), 2922 (w, C–H), 2900 (w, =C–H), 1546 (m, C=C), 1462 (s, N=C–C), 1368 (m, C=C–H), 1281 (w, C–N), 1207 (m, C=C–H), 737 (m, C=C–C), 696 (w, C–H).

2.2.2. Free ligand H_2TMTAA

The free ligand (free-base) was prepared from the NiTMTAA complex following the procedure outlined by Goedken and Weiss [4]. Yield of the yellow solid product: 55%. UV–vis (CH_2Cl_2) λ_{max} (molar extinction coefficients are given in parentheses, $\text{mol}^{-1} \text{L cm}^{-1}$); 254 nm (8200), 264 nm (7500) and 348 nm (16,300). Anal. calcd for $\text{C}_{22}\text{H}_{24}\text{N}_4$ (MM = 344.46 g/mol) C, 76.7%; H, 7.0%; N, 16.3%. Found C, 76.9%; H, 6.8%; N, 15.6%. $^1\text{H NMR}$ (CCl_4); δ 2.1 ppm (12H), δ 4.9 ppm (2H) and δ 7.0 ppm (8H); FT-IR (KBr, cm^{-1}): 3062 (w, =C–H), 3040 (w, C=C), 2922 (w, C–H), 2900 (w, =C–H), 1616 (s, C–N–H) 1548 (m, C=C), 1510 (w, N=C–C), 1383 (s, =C–H), 1275 (w, C–N), 1190 (w, C–H), 752 (m, C=C).

2.2.3. $[\text{Mn(III)}(\text{TMTAA})]\text{NCS}$

Initially the thiocyanate bis (acetylacetonate) manganese(III) was synthesized following the procedure outlined by Marianelli and Stults [26]. The crystallized product was filtered and dried under vacuum (yield 85%). $\text{C}_{11}\text{H}_{14}\text{NO}_4\text{SMn}$ (MM = 311.14 g/mol); mp 169–170 °C. FT-IR (KBr, cm^{-1}): 3010 (w, C–H), 2073 (s, C \equiv N), 1535 (s, C \cdots C + C \cdots O), 1421 (m, C \cdots O + C \cdots C), 1342 (s, C–H) 1284 (m, C–CH $_3$ + C \cdots C), 1032 (m, CH $_3$), 949 (m, C \cdots C + C \cdots O), 798 (m, C–H, C–S), 630 (w, Mn–O), 489 (s, Mn–O), 432 (w, NCS).

The $[\text{Mn}(\text{TMTAA})\text{NCS}]$ was synthesized from the manganese salt (thiocyanate bis(acetylacetonate) manganese(III)) following the procedure outlined by Neves and Dabrowiak [27a]. Yield: 65%. UV–vis (CH_2Cl_2) λ_{max} (molar extinction coefficients are given in parentheses, $\text{mol}^{-1} \text{L cm}^{-1}$); 274, 358 nm (34,000), 462 and 604 nm (2400). $\text{C}_{23}\text{H}_{22}\text{N}_5\text{SMn}$ (MM = 455.22 g/mol). FT-IR (KBr, cm^{-1}): 3062 (w, =C–H), 3040 (w, C=C), 2922 (w, C–H), 2900 (w, =C–H), 2054 (s, C \equiv N), 1531 (s, C=C), 1460 (m, N=C–C), 1383 (s, =C–H), 1279 (m, C–N), 1194 (m, C–H), 752 (m, C=C), 432 (w, NCS).

2.2.4. $\text{NiCl}_2\text{TMTAA}$

The Ni(II) macrocycle was synthesized following the procedure outlined by Goedken and Weiss [4]. 4-Chlorophenylenediamine, 2,4-pentanedione and nickel acetate tetrahydrate were reacted in methanol during 38 h to produce the $\text{NiCl}_2\text{TMTAA}$. This reaction was monitored by

the UV–vis analysis through the observed changes at 272 and 400 nm [25]. Yield: 48%. UV–vis (CH_2Cl_2) λ_{max} (molar extinction coefficients are given in parentheses, $\text{mol}^{-1} \text{L cm}^{-1}$); 272 nm (36,500), 336 nm (11,600), 400 nm (39,800), 432 nm (17,400) and 592 nm (7400). Anal. calcd for $\text{C}_{22}\text{H}_{20}\text{Cl}_2\text{N}_4\text{Ni}$ (MM = 470.02 g/mol) C, 60.8%; H, 4.8%; N, 12.5%. Found C, 59.3%; H, 4.3%; N, 11.9%. $^1\text{H NMR}$ (CCl_4); δ 2.1 ppm (12H), δ 4.9 ppm (2H) and δ 6.6 ppm (6H). FT-IR (KBr, cm^{-1}): 3070 (w, C–H), 2959 (w, C–H), 2923 (w, C–H), 2848 (w, C–H), 1541 (m, C=C), 1460 (s, CH $_3$), 1390 (s, CH $_3$), 1274 (w, C–N), 1207 (m, C–CH $_3$), 856 (m, C–H), 800 (m, C–H), 777 (m, C–H) and 582 (w, C–Cl).

2.2.5. $\text{NiCl}_4\text{TMTAA}$

The Ni(II) macrocycle was synthesized following the procedure outlined by Goedken and Weiss [4]. 4,5-Dichlorophenylenediamine, 2,4-pentanedione and nickel acetate tetrahydrate were reacted in methanol during 35 h to produce the $\text{NiCl}_4\text{TMTAA}$. This reaction was monitored by the UV–vis analysis through the observed changes at 274 and 404 nm [25]. Yield: 14%. UV–vis (CH_2Cl_2) λ_{max} (molar extinction coefficients are given in parentheses, $\text{mol}^{-1} \text{L cm}^{-1}$); 274 nm (37,400), 350 nm (10,700), 402 nm (43,700), 436 nm (21,300) and 592 nm (8400). $\text{C}_{22}\text{H}_{18}\text{Cl}_4\text{N}_4\text{Ni}$ (MM = 538.91 g/mol). $^1\text{H NMR}$ (CCl_4); δ 2.1 ppm (12H), δ 4.9 ppm (2H) and δ 6.6 ppm (4H). FT-IR (KBr, cm^{-1}): 2965 (w, C–H), 2924 (w, C–H), 2855 (w, =C–H), 1562 (w, C=C), 1530 (m, C=C), 1450 (s, N=C–C), 1391 (s, =C–H), 1273 (m, C–N), 1211 (w, =C–H), 1134 (m, C–H), 1036 (m, C–H), 808 (m, =CHR), 623 (m, C–Cl).

2.3. Immobilization of metallotetraazaannulene in PVG plates

The immobilization of NiTMTAA or $[\text{Mn}(\text{TMTAA})\text{NCS}]$ in PVG was carried out by three different methods, by immobilization in Vycor plate (10 mm \times 10 mm \times 1 mm). In order to facilitate the identification, the products obtained were named by the nomenclature MT-PVGX, where M = Ni(II) or Mn(III), T = the complex TMTAA, PVG = porous Vycor glass and X = 1, 2, 3 the number of the method used for monitoring the reaction process.

2.3.1. Method 1 (compounds obtained – NiT-PVG1 and MnT-PVG1)

A plate of PVG was immersed in a 1.0 cm path length UV–vis quartz cuvette (40 mL of volume capacity) containing 20 mL of metallomacrocylic dichloromethane solution ($4 \times 10^{-4} \text{ mol L}^{-1}$). The cuvette was closed and the supernatant solution was monitored by UV–vis spectroscopy during 800 h. After this period the plate was removed from the solution, exhaustively washed with dichloromethane, methanol and acetonitrile in a Soxhlet extractor and stored under Ar for later analysis.

2.3.2. Method 2 (compounds obtained – NiT-PVG2 and MnT-PVG2)

A plate of PVG was added to a flask containing 20 mL of metallomacrocyclic dichloromethane solution ($5 \times 10^{-4} \text{ mol L}^{-1}$) at room temperature. The flask was maintained closed, but the PVG plate was removed periodically from the solution, analyzed by UV–vis spectroscopy and EPR, and dipped again in the solution. The immobilization process was maintained for 250 h when the plate was removed from the solution, exhaustively washed with dichloromethane, methanol and acetonitrile in a Soxhlet extractor and stored under Argon.

2.3.3. Method 3 (compound obtained – MnT-PVG3)

A plate of PVG was added to a closed flask containing 20 mL of dichloromethane solution of $[\text{Mn}(\text{TMTAA})\text{NCS}]$ ($5 \times 10^{-4} \text{ mol L}^{-1}$) at room temperature for 2 h. The plate was removed from the solution, washed with dichloromethane, air dried and analyzed by EPR and UV–vis spectroscopy.

2.4. Homogeneous catalytic reaction

Bromocyclohexane, chlorocyclohexane and iodocyclohexane reduction reactions with NaBH_4 were carried out in a 2 mL glass borosilicate vial with an open top screw cap containing a silicone–Teflon-faced septum. The catalyst NiTMTAA ($2.5 \times 10^{-3} \text{ mol L}^{-1}$) and NaBH_4 (1:1–1:100 NiTMTAA: NaBH_4 molar ratio) were mixed under argon atmosphere at room temperature and followed by the addition of 900 μL of solvent (acetonitrile or diglyme) and 100 μL of ethanol (used as hydrogen donor). The solvents used were previously stored under argon. The reaction was initiated by the addition of the substrate (bromocyclohexane, chlorocyclohexane or iodocyclohexane). The mixture was stirred at room temperature for 2 or 3 h in the absence of light. The reaction products were analyzed by gas chromatography (Shimadzu CG-14B gas chromatograph) equipped with a flame ionization detector and with a DB-WAX capillary column (J&W Scientific). The amount of products was determined by using 1-octanol or cyclohexanol as the internal standard. Each reaction was performed at least twice or more and the mixture was analyzed three times by GC. Control reactions without catalyst were performed.

2.5. Heterogeneous catalytic reaction

The iodocyclohexane reduction reaction with NaBH_4 was carried out in a 2 mL vial with an open top screw cap containing a silicone–Teflon-faced septum. The catalysts solid (NiTMTAA-PVG plate powdered in a mortar) and NaBH_4 (1:10 and 1:100 catalyst: NaBH_4 molar ratio) were mixed under argon atmosphere at room temperature and then 450 μL of solvent (diglyme) and 100 μL of ethanol (used as hydrogen donor) were added. After the substrate addition, the mixture was stirred at room temperature during 3 h in the absence of light. The products of the reaction were separated from the

solid catalyst by exhaustive washing and centrifugation of the solid with acetonitrile as solvent. The extracted solution was analyzed by GC following the same procedure used in homogeneous catalysis. The same procedure was followed in the control reactions using: (a) only the substrate, (b) substrate + NaBH_4 and (c) substrate + NaBH_4 + hydrogen donor. No products were detected in the control reactions.

2.6. Investigation of intermediate species

In order to study the intermediate species produced by the reaction of NiTMTAA and NaBH_4 , the reaction mixture was prepared following the procedure described in Section 2.4 without the addition of a substrate. The reaction was analyzed by EPR (at 77 K) and UV–vis (at room temperature) in a controlled period of time. After this period the substrate (iodocyclohexane) was added and the solution analyzed again.

3. Results and discussion

3.1. Immobilization of metallotetraazaannulene in PVG plates

The porous Vycor glass acts as a cation exchanger due the presence of silanol groups in its surface which facilitate the diffusion and adsorption of cationic complexes, like $[\text{Mn}(\text{TMTAA})]^+$. The interaction of neutral complexes such as NiTMTAA is also possible by the van der Waals interaction. As expected, the anionic complexes are electrostatically repelled, as previously described by Gafney [28].

During the immobilization process, the glass plate immobilized with both manganese and nickel tetraazaannulene acquires a green color characteristic of complexes solutions. For the NiTMTAA complex, the solid NiT-PVGX ($X=1, 2$) retains the green color for months after the immobilization process, which indicates the expected stability of the nickel complex in the porous glass. However, the same stability was not observed for the manganese complex. The color of the MnT-PVGX ($X=1, 2, 3$) solid changed to red after few hours [27].

The UV–vis spectra of metallotetraazaannulene complexes showed absorption bands in the range of 270–650 nm. The weaker bands at 592 and 604 nm (Ni complex and Manganese complex, respectively) are assigned to ligand-to-metal charge transfer (LMCT). The intense peaks observed at 398 and 358 nm (Ni complex and Manganese complex, respectively) are associated to $\pi \rightarrow \pi^*$ ligand transition [29,30].

The electronic spectra changes observed for the metallotetraazaannulene solutions used for impregnation (Method 1) are shown in Fig. 2a (NiT-PVG1) and 2b (MnT-PVG1). The intense decrease of the LMTC bands at 592 nm (nickel compound) and 604 nm (manganese compound) was observed with the increase of the immobilization time (Fig. 2), which suggests the migration of molecules through glass pores. It was observed that the immobilization rate of MnTMTAA is

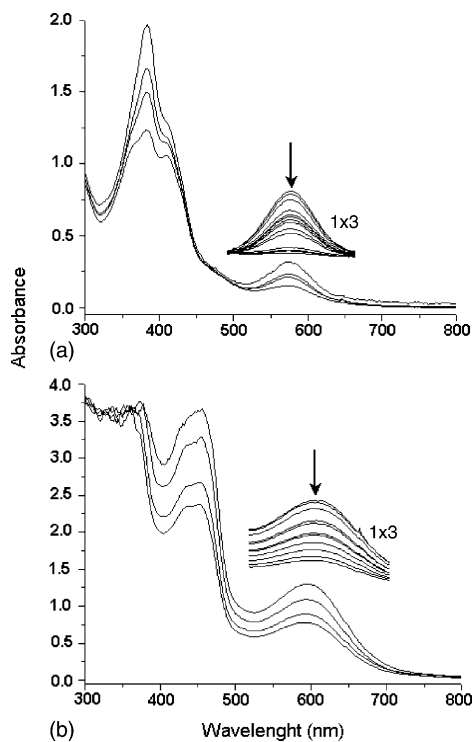


Fig. 2. UV-vis spectra of immobilization solution used in the Method 1: (a) NiTMTAA solution (to obtention of NiT-PVG1); (b) Mn(TMTAA)NCS solution (to obtention of MnT-PVG1).

higher than NiTMTAA. The immobilization was stopped for MnTMTAA after 170 h against 770 h for the Ni(II) complex (observed by the colorless solutions and absence of modification in the UV-vis spectra). The higher immobilization rate for the cationic MnTMTAA may be due to its higher interaction with the PVG charged pore surface.

The UV-vis spectra of the impregnated PVG plates obtained by the second method (NiT-PVG2 and MnT-PVG2) are presented in Fig. 3. The increase in intensity of the characteristic bands of nickel complex during 225 h confirms the immobilization (Fig. 3I). After 87 h of immobilization the color of the PVG plate immersed in the solution of nickel compound NiT-PVG2 remained a dark green color, confirming the stability of nickel complex into the PVG plate.

In contrast with what was observed in NiT-PVG2, an intensity increase of characteristic bands of the Mn(III) was not observed in the spectra of the MnT-PVG2 (Fig. 3II). Instead it an intensity increase in the spectrum was observed without definition of bands. Simultaneously, a change in the plate color (MnT-PVG2) was observed. During the first 3 h of immobilization the plate remained green (the characteristic color of the MnTMTAA), but after 24 h (with the plate kept inside the immobilization solution) the color changed to dark red suggesting that a decomposition process had been occurring simultaneously with the immobilization process. The decomposition process was confirmed by EPR analysis of the compound MnT-PVG2 after the immobilization reaction. The decomposition of Mn(III) complex must have occurred

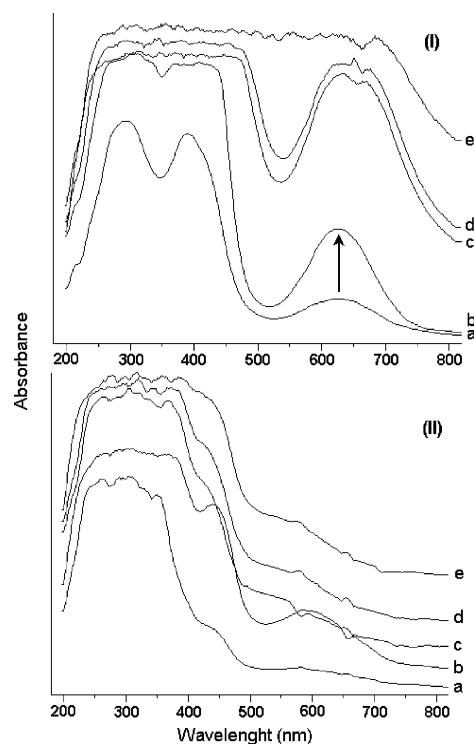


Fig. 3. UV-vis spectra of PVG plate used in the Method 2 to (I) NiT-PVG2; (II) MnT-PVG2, in different times: (a) 1 h, (b) 15 h, (c) 24 h, (d) 87 h and (e) 225 h.

after the immobilization inside the glass pores based on the fact that in the first method of immobilization (Method 1) the original complex solution had not shown spectral changes indicating alterations in the original complex (Fig. 2b).

The EPR spectra of the MnT-PVG1 and MnT-PVG2 plate samples are shown in Fig. 4a and b. Both spectra presented EPR signals with six lines typical of octahedral high spin, d^5 , $S = 5/2$ Mn(II) mononuclear complexes [31]. Since the [Mn(III)TMTAA(NCS)] solid spectrum was EPR silent (as expected in manganese(III) ion with an electronic configuration $3d^4$ and nuclear spin(I) $5/2$), the spectra presented in Fig. 4 indicates that the Mn(III) ions were reduced during the immobilization process to obtain the MnT-PVG1 and MnT-PVG2. Few examples of Mn(III) (d^4) complex EPR spectra are observed [31]. The silent EPR spectrum characteristic of Mn(III) compounds is explained by the zero field splitting for the levels ± 2 , ± 1 and 0 which leads to four transitions when the splitting is small, and none when the splitting is large. As expected the [Mn(III)TMTAA(NCS)] does not show EPR spectrum due the Jahn-Teller distortions allied to the large zero field splitting.

The solids NiT-PVG1 and NiT-PVG2 have shown the expected EPR silent spectra since the Ni(II) has an electronic configuration pair, as low spin and high spin [31] and tetraaza[14]annulene is a neutral ligand, neither the metal nor the ligand can produce an EPR signal.

After immobilization (Methods 1 and 2), the compounds NiT-PVG1, MnT-PVG1, NiT-PVG2, MnT-PVG2

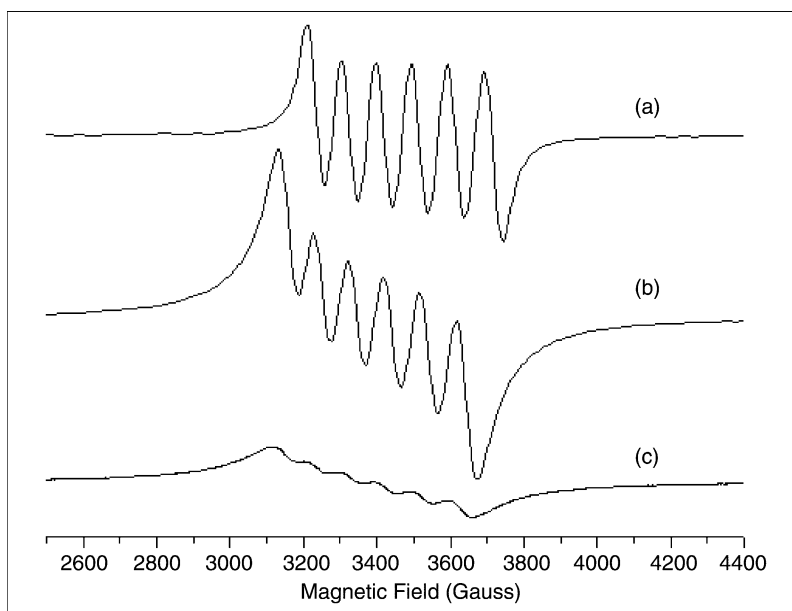


Fig. 4. EPR spectra of hybrid material of PVG and Manganese tetraaza; (a) MnT-PVG1 after 24 h from immobilization process; (b) MnT-PVG2 after 24 h from immobilization process; (c) MnT-PVG1 after the washing process on Soxhlet extractor.

were washed in Soxhlet extractor, in order to verify the retention capacity of complexes inside the glass. Both Nickel complexes (NiT-PVG1 and NiT-PVG2) remained impregnated with the PVG even after the plates had been washed for 6 h in methanol, dichloromethane and acetonitrile. A small amount of NiTMTAA complex was observed in the washing solution obtained from NiT-PVG1 and NiT-PVG2, due to the complexes immobilized on the external surface of PVG. However, in the MnT-PVG1 and MnT-PVG2 plates washed with methanol, dichloromethane and acetonitrile a light yellow color was detected in the washing solution and the PVG plates became bleached. The yellow color of the solution was not noticeable among the characteristic bands of the MnTMTAA. The EPR spectrum of the MnT-PVG1 plate sample, after the washing process in Soxhlet extractor, is shown in Fig. 4c. This spectrum presented EPR signal with six lines typical of Mn(II), suggesting that the Mn(II) ion remained immobilized in the PVG plate.

In order to monitor the manganese complex inside the PVG pores, compound MnT-PVG3 (using the Method 3) was produced. The PVG plate was maintained inside the [Mn(III)TMTAA(NCS)] solution for only 2 h and was removed for UV–vis and EPR analyses. The UV–vis spectrum recorded at 20 min after the PVG removal from the solution showed the characteristic bands of Mn(III) complex at 358 and 604 nm [27] (Fig. 5a) indicating that the manganese III complex was apparently intact inside the PVG pores. The corresponding EPR spectrum was silent, as expected from Mn(III) with an electronic configuration $3d^4$ and nuclear spin(I) $5/2$ [31]. After 1.5 h, the intensity of the bands in the manganese complex decreased and the EPR spectrum showed a signal characteristic of Mn(II) (Fig. 5b). The changes of

the electronic and EPR spectra were monitored for 140 h (Fig. 5c–e). After this time the MnT-PVG3 was completely red, the UV–vis spectrum has not shown bands of Mn(III) complex and the EPR signal characteristic of Mn(II) d^5 pre-

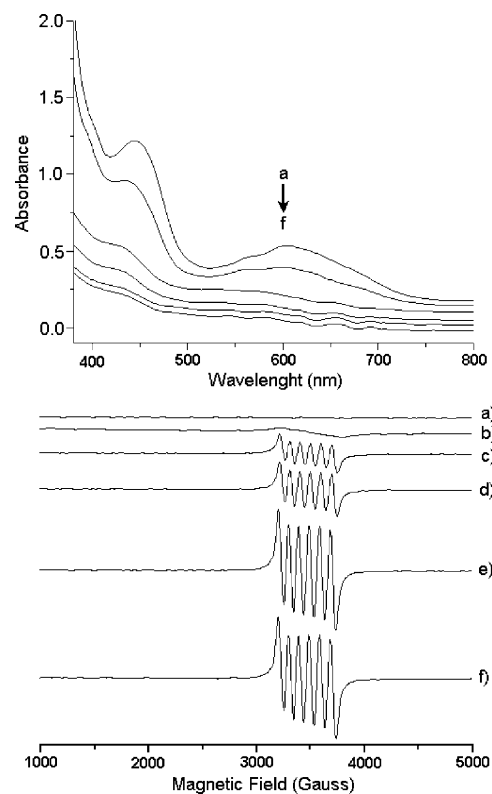


Fig. 5. UV–vis (top) and EPR (bottom) spectra of MnT-PVG3 in different times of air exposure after the impregnation time: (a) 20 min, (b) 1.5 h, (c) 24 h, (d) 41 h, (e) 66 h and (f) 144 h.

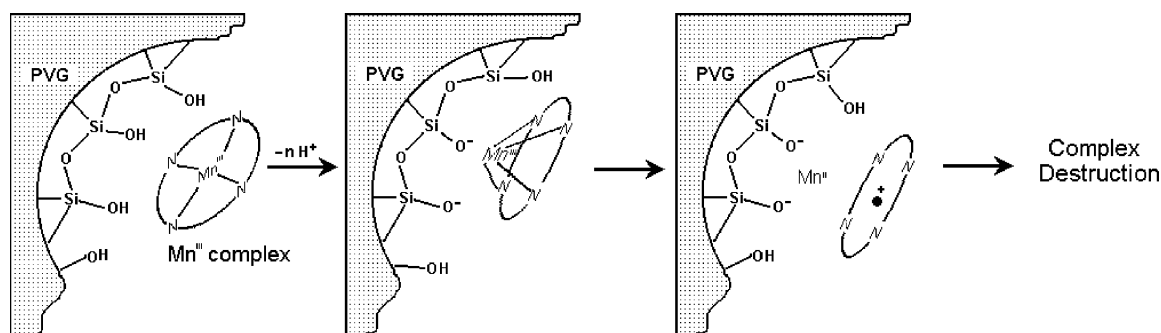


Fig. 6. Schematic proposition of Mn(TMTAA) degradation into PVG porous.

sented the maximum intensity, confirming a decomposition process (Fig. 5f).

The instability of [Mn(TMTAA)NCS] inside the porous glass may be related to the Mn(III) complex structure and charge. The manganese(III) complex has a positive charge that is neutralized by a counter-ion like NCS⁻. Inside the porous systems, the positive charge can be stabilized by Si–O⁻ surface groups coordinated axially to the manganese (III) ion. The axial coordination promotes the displacement of the Mn(III) from the equatorial ring in a similar way observed in manganese porphyrins which interact with methanol. This interaction promotes the reduction of Mn(III) to Mn(II) [32]. Schultz attributed the absence of methanol as responsible for the slow kinetics of electro-reduction in manganese porphyrins. The large additional out-of-plane displacement of the Mn atom upon reduction from Mn(III) to Mn(II) in porphyrins promotes a lower inner-shell activation barrier to the electron transfer. This process can be occurring in the same way inside the pores. The easy reduction of the manganese can be promoted by the silanol groups coordinated axially to the Mn(III) ion. The manganese reduction is accomplished by the disappearance of the UV–vis characteristic bands of the macrocycle. This observation suggests that the metal reduction can promote the ligand oxidation, followed by the macrocycle destruction favored by the presence of acid protons, in porous surroundings as proposed in Fig. 6 [2]. This process can create, for example, the benzodiazapinium salt, as proposed by Jager and Goedken [2,4], by the macrocycle degradation of acid environment, and that process is followed by the change of solution color from green to brownish purple.

Once the Ni(II) complex is a neutral compound, the nickel(II) ion was strongly stabilized by the ligand dibenzotetraaza[14]annulene, and only van der Waals interactions are likely to be significant. A weak axial interaction with the silanol groups can occur but not in the same way of the manganese complex and no destruction of the nickel complex inside the porous Vycor glass was observed.

3.2. Catalytic reduction in homogeneous systems

The NiTMTAA complex was used as catalyst in the bromocyclohexane, chlorocyclohexane and iodocyclohexane reductive dehalogenation reactions with NaBH₄ to obtain the

product cyclohexane [6]. The initial test reactions were performed with the bromocyclohexane. The results are shown in Table 1 (run 1–3) and the reaction yields are expressed as percentages (based on NaBH₄).

In the initial reactions performed in acetonitrile (run 1–3), no alkane formation by the reductive dehalogenation of bromocyclohexane was detected. Arai et al. have shown that in the catalytic dehalogenation reaction a hydrogen donor source is necessary. They proposed that the reductive dehalogenation of substrates such as bromocyclohexane by the Ni(TMTAA)/NaBH₄ systems proceeds through an electron transfer from the metal-reduced NiTMTAA catalytic active species to the substrate followed by the nucleophilic substitution of the halide by the hydride coming from a hydrogen donor [6]. In the absence of ethanol as hydrogen donor the majority of cyclohexane was yielded by a radical reaction of NaBH₄ with the substrate. In fact, reactions performed in the presence of ethanol (run 4–8) have shown quite better results with production of cyclohexane. However, even in the presence of ethanol, better results were obtained only when the solvent diglyme was used instead of acetonitrile (run 8) probably due to the following facts: (a) diglyme facilitates the elimination of Br⁻ ions, (b) it is a better solvent for NaBH₄ and (c) it does not strongly coordinates with nickel. In the

Table 1
Reductive dehalogenation of bromocyclohexane with NaBH₄ catalyzed by NiTMTAA^a

Run	Molar ratio ^b (catalyst:red.:subst.)	Ethanol (%) ^c	Cyclohexane (%)	Turnover number ^d
1	1:100:100	0	Trace	0.3
2	1:50:100	0	Trace	0.2
3	1:10:100	0	<2.0	0.2
4	1:100:100	10	Trace	0.5
5	1:50:100	10	<2.0	0.3
6	1:10:100	10	<2.0	0.1
7	1:5:100	10	<2.0	0.1
8	1:10:100	10	7.0	0.7

^a To reaction condition see Section 2.4. All reactions were performed for 2 h using acetonitrile as solvent except the reaction number 8 that was performed for 3 h in diglyme solvent. The % yield was based on the NaBH₄.

^b Molar ratio of NiTMTAA:NaBH₄:bromocyclohexane.

^c Percentage of ethanol added to the solvent as hydrogen donor (v/v).

^d Turnover number = mol of yielded alkane/mol of NiTMTAA. Trace quantities mean that the yield was below to 1%.

Table 2
Reductive dehalogenation of iodocyclohexane with NaBH₄ catalyzed by nickel complexes^a

Run	Complex	Molar ratio ^b (catalyst:red.:subst.)	Ethanol (%) ^c	Cyclohexane (%)	Turnover number ^d
1	NiTMTAA	1:1:100	10	6	0.07
2	NiCl ₂ TMTAA	1:1:100	10	9	0.1
3	NiCl ₄ TMTAA	1:1:100	10	9	0.1

^a To reaction condition see Section 2.4. All reactions were performed for 2 h using acetonitrile as solvent. The % yield was based on the NaBH₄.

^b Molar ratio of NiTMTAA:NaBH₄:iodocyclohexane.

^c Percentage of ethanol added to the solvent as hydrogen donor (v/v).

^d Turnover number = mol of yielded alkane/mol of NiTMTAA, NiCl₂TMTAA (2.0×10^{-3} mol L⁻¹) and NiCl₄TMTAA (1.8×10^{-3} mol L⁻¹).

Table 3
Reductive dehalogenation of iodocyclohexane with NaBH₄ catalyzed by NiTMTAA^a

Run	Solvent	Molar ratio ^b (catalyst:red.:subst.)	Ethanol (%) ^c	Cyclohexane (%)	Turnover number ^d
1	Acetonitrile	1:10:100	10	23	2.5
2	Diglyme	1:10:100	10	76	8.1

^a To reaction condition see Section 2.4. All reactions were performed for 3 h. The % yield was based on the NaBH₄.

^b Molar ratio of NiTMTAA:NaBH₄:iodocyclohexane.

^c Percentage of ethanol added to the solvent as hydrogen donor (v/v).

^d Turnover number = mol of yielded alkane/mol of NiTMTAA.

diglyme solution an increase of the turnover number (run 8) in comparison with reactions in acetonitrile (run 6) was observed.

The familiar flexible structure of the NiTMTAA compound is an important property for its catalytic activity [6,8]. In fact, the ruffled structure has been related to the potential biomimetic use of the complex [5,8]. The addition of substituent groups to the macrocycle structure such as halogens, or organic radical groups such as methyl and ethyl, can accentuate this framework distortion and facilitate the formation of intermediate species with nickel(I) involved in the catalytic process [8]. In order to investigate this process the compounds Ni(Cl₂TMTAA) (2.0×10^{-3} mol L⁻¹) and Ni(Cl₄TMTAA) (1.8×10^{-3} mol L⁻¹), Fig. 1c and d, respectively, were used as catalysts in the bromocyclohexane homogeneous dehalogenation reaction (Table 2). The results showed a small increase of cyclohexane yield using these macrocycle catalysts if compared to NiTMTAA in the same reaction condition. These facts suggest that the catalytic activity can possibly be modulated by the addition of appropriate substituents to the TMTAA framework in order to generate active intermediate species [8].

When the chlorocyclohexane, a substrate that shows a lower reactivity in a nucleophilic substitution reaction, was used in the same conditions as run 8 in Table 1, no alkane yield was observed [33]. However, for the iodocyclohexane, a more reactive compound, better results of dehalogenation were observed (Table 3). In diglyme, a 76% conversion of iodocyclohexane to cyclohexane was observed (Table 3, run 2). That difference in the reduction reaction between bromocyclohexane, chlorocyclohexane and iodocyclohexane occurs due the basicity difference of their conjugate bases (Cl⁻, Br⁻, I⁻) formed in the reaction catalyzed by tetraaza complexes. For example, the iodocyclohexane has a high reactivity because its conjugate base is very weak, so the reduction reaction of iodocyclohexane is faster than other alkyl halides [33].

3.3. Catalytic reduction in heterogeneous systems

Although the use of dibenzotetraaza[14]annulene compound as a biomimetic model of Factor F₄₃₀ in the reductive dehalogenation of alkyl halide [6] was already reported, the use of the immobilized tetraaza compounds as catalyst of reductive reaction in heterogeneous catalysis was not studied. The possibility of separation of the catalyst, at the end of the reaction, from the organic constituents of the reaction mixture in order to promote its reuse in a new reaction, stimulated the study of the heterogenization of the catalyst inside the porous Vycor glass. The characteristics of this support e.g. high porosity, resistance and possibility of immobilization by van der Waals interaction motivated its choice. Besides that, it is observed that the structure of the material can also contribute to the selectivity of the catalytic reaction [10].

The compound NiT-PVG1 was used as model for Factor F₄₃₀. Similar conditions of those used in the homogeneous reactions were used with the heterogeneous catalytic dehalogenation reaction of iodocyclohexane in diglyme solvent (run 1, Table 4). In this run the heterogeneous catalyst

Table 4
Reductive dehalogenation of iodocyclohexane with NaBH₄ catalyzed by NiT-PVG1^a

Run	Molar ratio ^b (catalyst:red.:subst.)	Ethanol % ^c	Cyclohexane (%)	Turnover number ^d
1	1:10:100	10	Trace	0.2
2	1:100:100	10	16	14
3 ^e	1:100:100	10	20	19

^a To reaction condition see Section 2.5. All reactions were performed for 3 h in diglyme solvent. The % yield was based on the NaBH₄.

^b Molar ratio of NiTMTAA:NaBH₄:iodocyclohexane.

^c Percentage of ethanol added to the solvent as hydrogen donor.

^d Turnover number = mol of yielded alkane/mol of NiTMTAA. Trace quantities mean that the yield was below to 1%.

^e Reuse reaction.

did not show catalytic activity in the dehalogenation reaction of iodocyclohexane. This result suggests that substrate access to the axial position of the nickel complex decreased by the immobilization process. When the catalyst reducing agent:substrate molar ratio was changed to 1:100:100 the cyclohexane yield increases (run 2, Table 4) showing that just only at higher concentrations can the substrate connect to the metal center. Although the new conditions improve the cyclohexane production, indicating that the NiTMTAA-PVG system is an interesting potential catalyst, the results were inferior to those obtained with the homogeneous systems showing that the determination of the ideal conditions for heterogeneous catalysis is not a trivial process. However, an important advantage of the immobilized-catalyst is the possibility of reutilization. The NiTMTAA-PVG solid was reutilized in a new reaction after having been recovered from the first reaction (run 3, Table 4) using the same conditions utilized in run 2, in this catalyst reutilization the cyclohexane yield increases from 16% to 20%. This observation can be indicative of the nickel tetraazaannulene compound resistance to the reaction conditions and of a strong interaction between the nickel compound and the support; the nickel complex is not released from the surface after the first utilization. In fact UV–vis analysis of the solution reactions mixtures showed that the NiTMTAA was not leached from the support during the reactions (none of the reaction solutions have shown the characteristic UV–vis bands in the spectra).

Despite of the poor catalytic results observed in heterogeneous catalytic reactions, the use of this catalyst is still interesting from the economic point of view based on the possibility of larger solid reutilization.

3.4. Investigation of the intermediate species

During the homogeneous catalytic dehalogenation reaction it was observed that the NiTMTAA complex solution changed from green to red and returned to green at the end of the reaction with a decrease of NaBH_4 concentration. The same color change was observed for the NiTMTAA-PVG system. The UV–vis spectrum of the red reaction solution produced by the reaction of the NiTMTAA with NaBH_4 was recorded (Fig. 7) and showed a band at 480 nm. Szalda et al. reported a similar spectrum for nickel tetraaza compounds when CO was introduced into the solution of nickel tetraaza, prepared in the presence of a reducing agent in CH_3CN under vacuum, and attributed the red color to species formed by the axial coordination of CO molecule to Ni(I) [34]. When the red solution was frozen at 77K and analyzed by EPR (Fig. 8A) an intense signal at $g = 2.12$ ($A = 24$ G) characteristic of Ni(I) species was observed [6]. A low intensity signal at $g = 2.01$ ($A = 22$ G) that was attributed to some contamination of the degradation product of NiTMTAA was also observed [25]. The EPR signal disappeared after the addition of substrate iodocyclohexane (Fig. 8b), suggesting that the Ni(I) species were consumed. The UV–vis and EPR data suggest that the Ni(I) species detected were formed as intermediate

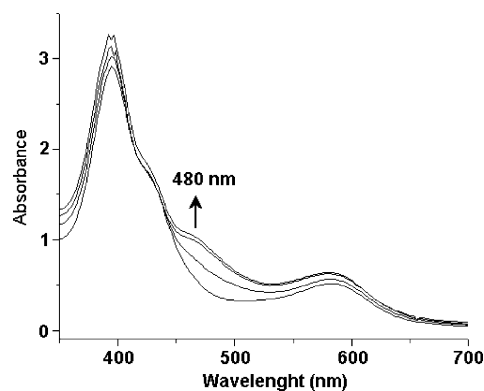


Fig. 7. UV–vis spectra of reaction environment for the homogeneous catalytic dehalogenation by NiT-PVG1.

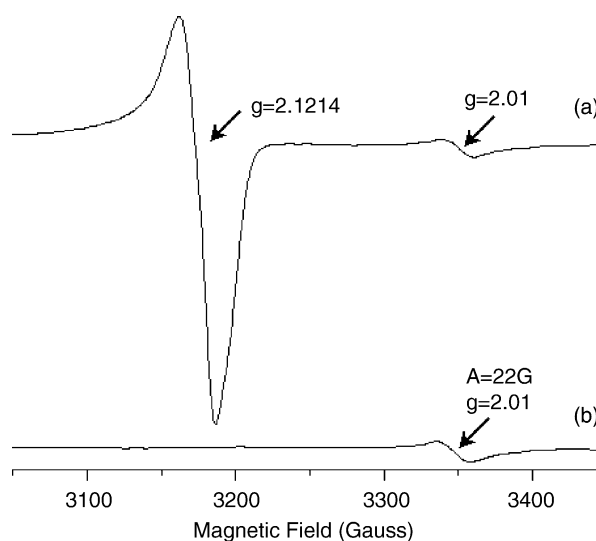


Fig. 8. EPR spectra of reaction environment for the homogeneous catalytic dehalogenation by NiT-PVG1 showing a intense signal characteristic of species Ni(I) (A) and the signal disappear after addition of Iodocyclohexane (B).

active specie in the dehalogenation reaction intermediated catalyzed by NiTMTAA complex. The same color change was observed when the PVG immobilized catalyst was used also suggesting the presence of Ni(I) intermediate specie in the heterogeneous catalysis. The EPR and UV–vis study of the PVG solid catalyst will be investigated soon.

4. Conclusions

In this paper we presented the study of interaction of Ni(II) and Mn(III) tetraaza[14]annulene inside the porous Vycor glass. The immobilization of the complexes was performed by three different methods. The high interaction of the Manganese complex was confirmed by the greater immobilization rate to the cationic complex. However, the interaction of silanol groups with manganese complex promoted the degra-

dation of tetraaza[14]annulene and the reduction of Mn(III) to Mn(II). The decomposition of Mn(TMTAA) was accompanied by the decrease of its UV–vis and EPR signals. The NiTMTAA was not degraded inside the PVG pores and remained immobilized producing a hybrid material comprised of the nickel complex and PVG, promoting the studies of heterogeneous catalytic activity as a model for Factor F₄₃₀.

The NiTMTAA exhibits a remarkable catalytic activity for the reduction of Iodocyclohexane by NaBH₄, with conversion of 76%. However, the catalytic efficiency of the NiT-PVG1 system for Iodocyclohexane reduction was smaller than that observed for NiTMTAA in homogeneous catalysis. In spite of this fact, the NiT-PVG1 has an important advantage over the homogeneous system, the reutilization possibility. For the reutilization tests, the NiT-PVG1 shows appreciable activity, with formation of cyclohexane at 20%.

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