CONTENT
(according to the full thesis)

Introduction

Catalytic processes are successfully used in the chemical, petroleum, food or pharmaceutical industries, etc. Over 90% of the commercial chemicals involve the use of catalysts, at least in one of the synthesis steps. The development of these processes has led to a continuous diversification of the catalytic materials, consisting of extremely varied chemical compositions and textures, which respond to the kinetics of the process. Also, these processes should take into account the environmental quality principles, procedures which are requiring more rigorous control of the conditions in which chemical processes and waste management take place. In this context, priority is given to the use of less toxic materials and intermediates, where is mandatory the replacement of highly degradable materials with biodegradable ones or the use of catalysts with activity, but especially with higher selectivity into the considered processes.

Catalytic hydrogenation reactions have an important contribution to supporting and developing the priorities outlined above. Hydrogenation by a non-catalytic process is usually carried out at very high temperatures and/or pressures, requiring the activation of both the hydrogen and the chemical group that is subjected to hydrogenation. Hydrogenation reactions can occur **i)** by the dissociative addition of hydrogen at a chemical element, to a homogeneous unsaturated chemical bond (double, triple or aromatic ring) or heterogeneous (C=O from carbonyl or carboxyl derivatives, N=O from nitro derivatives etc.)[1] and **ii)** in the presence of molecules able to transfer hydrogen such as alcohols, cyclohexene or cyclohexadiene and their derivatives, hydrazine, formic acid and its salts, etc.[2] Type **ii**) reactions are also known in the literature as hydrogen transfer reactions.

Catalytic hydrogenation reactions may be carried out **i)** in *homogeneous systems*, conditions in which the catalyst and reactants are dispersed in the same phase, at the molecular level; their access to the active centers takes place easily, but the separation of the catalyst from the reaction products is difficult[3] and **ii)** in *heterogeneous systems*, conditions in which the catalyst and the substrate are in different phases; in this case, the catalyst is readily separable from the reaction mixture, while the access of the substrate to the catalytic active centers is limited.[4]

The purpose of this thesis was to identify new porous supports with or without noble metal content, used to design selective catalysts for hydrogenation reactions in order to synthesize more valuable chemical compounds of great importance for both industry and fine chemicals synthesis processes. In order to achieve this objective, we pursued: **i)** the synthesis of catalysts using carbon-based materials (noble metal free graphene, active carbon and polymer organic frameworks such as covalent organic frameworks (COF) or porous organic polymers (POP) – which are easily recoverable from the reaction medium **ii)** the synthesis of catalysts containing Au and/or TiO_2 using a mesoporous SiO_2 support type UVM-7 **iii)** the complete characterization of the prepared catalysts by complementary techniques: TG-DTA adsorption-desorption isotherms of N_2 at - 196 °C, XRD, XPS, ATR-FTIR, Raman, UV-VIS, TEM, STEM-HAADF, AFM, ICP-OES, H_2-TPR, H_2-TPD, NH_3-TPD, temperature programmed desorption measurements of 4-nitrostyrene, H_2, NH_3 or CO_2 chemisorption measurements - with the purpose of monitoring the structural and textural parameters of the support before and after the noble metal addition, **iv)** testing the synthesized catalysts for liquid phase selective hydrogenation reactions in heterogeneous systems; **v)** the identification and the quantification of the hydrogenation products obtained starting from different molecules containing at least two unsaturated functional groups, namely: 3-nitrostyrene, 4-nitrostyrene, trans-beta-nitrostyrene, 4-ethylnitrobenzene, 5-nitro-1-nitrocyclohexene, 4-nitrophenol, 4-nitroacetophenone, 1,2-naphthoquinone, 4-bromobenzophenone, 7-nitro-1-tetralone, acetophenone and **vi)** studying the relationship between the catalyst structure and its selectivity into the hydrogenation reactions of the above mentioned compounds.

The thesis is organized in six chapters, the first chapter being dedicated to the critical analysis of the results published in the literature concerning the selective heterogeneous catalytic systems used for hydrogenation reactions of unsaturated compounds containing several reducible groups in the structure, as well as the use of carbon-based materials as supports for the synthesis of active and selective catalysts into these processes. The second chapter describes the working premise, the characterization techniques used and the catalytic test protocol. The last four chapters present the analysis of the experimental results related to the use of new porous supports in the synthesis of selective catalysts in hydrogenation reactions.

The results of this research represent an original contribution to the design and development of novel selective catalysts, especially carbon-based materials, used in the hydrogenation reactions of various substrates containing at least two unsaturated functional groups in the molecule, with particular importance in the synthesis of fine chemicals.

CHAPTER I

Selective hydrogenation reactions in heterogeneous catalysis. Carbon-based catalytic materials. Structure-selectivity relations.

The literature study presented in Chapter I considered the following directions: Selective hydrogenation reactions in heterogeneous catalysis, carbon-based catalytic materials and selectivity-structure relations for selective hydrogenation reactions.

Catalytic hydrogenation reactions are generally associated with catalysts which contain at least one metal in their composition exhibiting catalytic activity and selectivity in the considered reaction.[5] The metal which is the catalytic active phase, is often deposited on the surface of a support, for better dispersion. The support used is desirable to be inert in the catalytic process, to have low cost and high specific surface area (SSA).

Following the literature study, we found that carbon catalysts are increasingly used as catalysts because of the structural and textural properties they possess. In fact, the study of carbon-based materials used as catalysts in various reactions unleashes a new branch of the catalysis known as carbocatalysis. The properties that recommend these materials in the synthesis of new catalysts: are specific high surfaces (1000 m^2/g),[6] high temperature resistance, easy separation, recycling and low manufacturing costs.

The allotropic carbon phases most commonly used as catalysts are: active carbon, graphite and graphite materials such as graphene, nanotubes and fullerenes. In the literature, however, there are numerous examples in which carbon-based materials have been used as supports for different metals.[8, 9] For example, graphene has been successfully used as a support for the synthesis of Ru nanorods type catalysts.[9] The catalytic performance of these materials has been investigated in the hydrogen transfer reaction for a wide range of carbonyl compounds. For the specific case of acetophenone (ACP), it was selectively reduced to 1-phenylethanol (100% conversion, 95% selectivity).

An interesting category of carbon-based materials recently used as catalytic supports are **porous organic frameworks**,[10, 11] of which COF and POP polymers are involved.[12] They have a high specific surface area, a well-defined pore structure and a high gas storage capacity such as H_2, CO_2, CH_4. The first article describing this type of material was published in 2005 by Adrien Cote et al.[10]

Cardenas-Lizana, in 2013, presents a study[13] on the use of polymer matrices as a support for metal nanoparticles in designing catalysts for the hydrogenation reaction of substituted nitro derivatives in the para position. According to this study, the polymeric matrix promotes the formation of a very well dispersed metal nanoparticle (NP) layer integrated into the polymeric network, thus preventing agglomeration and solubilization of the catalytic active phase after several reaction cycles (Figure I.1).

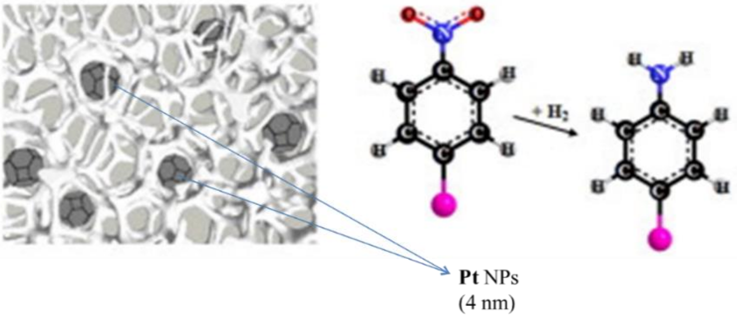


Figure I.1. COF as a catalytic support for Pt-catalyst nanoparticles for the hydrogenation reaction of para-chloronitrobenzene*[13]*

In another example, Ishida et al.[14] synthesized microporous polymeric meshes with Pd incorporated in the framework using a Pd catalyst (see Figure I.2). The resulting Pd/CMP catalyst proved to be active in the selective hydrogenation reaction of 4-nitrostyrene (4-NS) to 4-ethylnitrobenzene (4-EN).

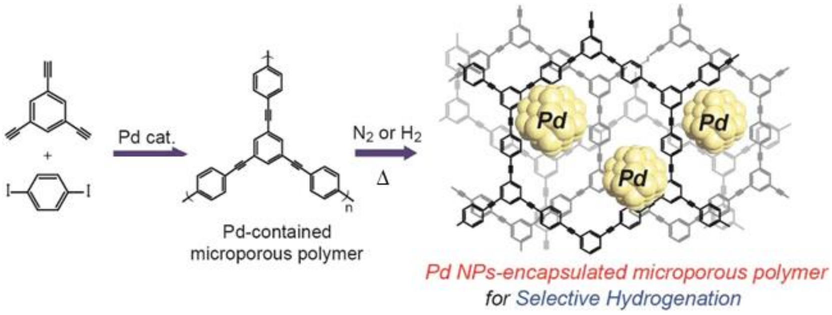


Figure I.2. COF as catalytic support for Pd nanoparticles and catalyst for the hydrogenation reaction of 4-nitrostyrene[14]

The challenges in the case of catalytic hydrogenation reactions in the presence of heterogeneous catalysts remain related to selectivity: chemo-, regio- and stereoselectivity, respectively. To improve this, there is a certain "design" of the catalyst that responds to the type of functionality that is desired to be hydrogenated, and this can be achieved by the controlled arrangement, at atomic level, of the active species. In this way, the selectivity is oriented both by a well-controlled chemisorption and by superficial diffusion. Also, in the case of catalytic hydrogenation reactions, materials such as i) Ni-Raney which are pyrophoric and require special storage and handling conditions, ii) platinum metals in high concentrations (1-5 wt%) or iii) other transition metals, which are exhaustible resources, are frequently used.

In support of the above, and taking into account environmental regulations, it is necessary to implement a sustainable chemistry. The literature study shows that carbon-based materials come in sustenance of such chemistry and they can fairly respond to the requirements for a stable support material with a high specific surface area, which can be used in the synthesis of stable, active and selective heterogeneous catalysts for hydrogenation reactions.

CHAPTER II

The working hypothesis. Characterization techniques. Catalytic tests.

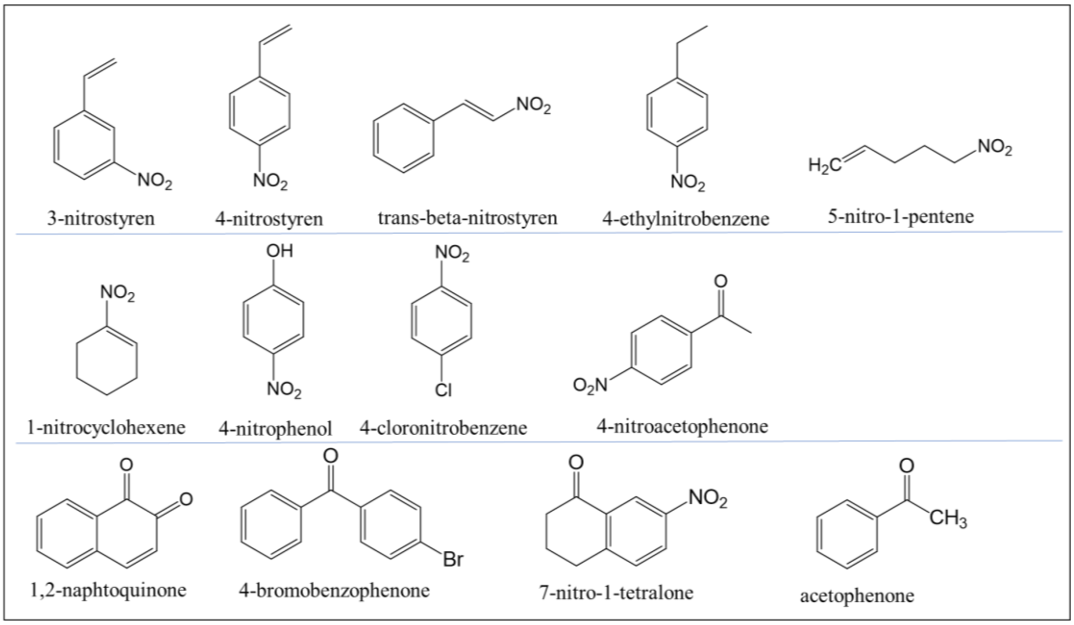
Chapter II describes the working hypothesis, the characterization techniques used and the way the catalytic tests were performed.

The objective of this thesis consisted in the study and synthesis **of catalysts based on new porous supports, active and selective** for hydrogenation reactions and in the study the relationships between the **catalyst structure** and its **selectivity** to a particular reaction product.

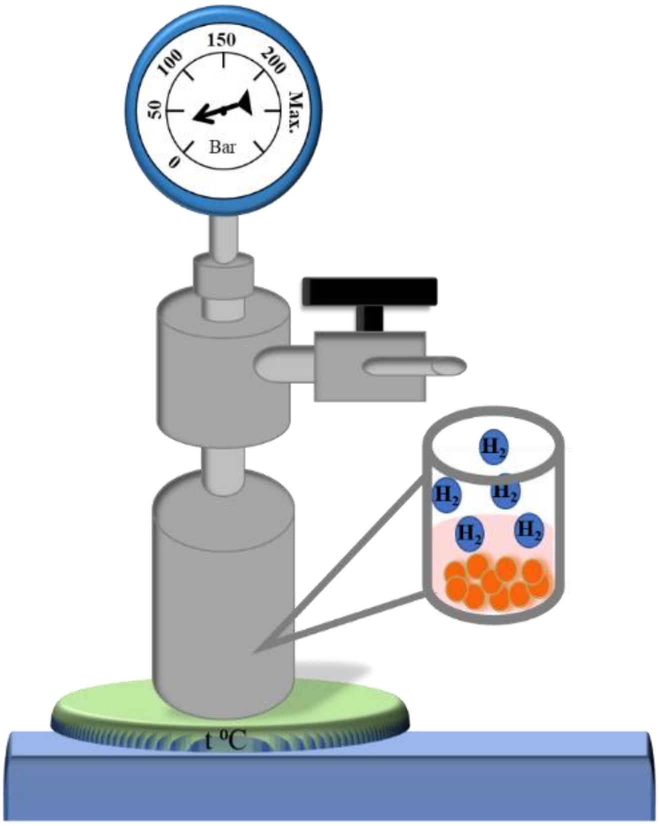
Taking into account the conclusions of the literature study, for the experimental part of this thesis, as a working hypothesis, the following were proposed:

a) the synthesis of heterogeneous catalysts using carbon-based materials as supports (graphene, commercial activated carbon (Sigma), covalent organic frameworks (COF) and porous organic polymers (POPs)) and mesoporous textured materials containing UVM-7 type silica and/or TiO_2. All of these materials were tested in hydrogenation reactions or were used as catalytic supports for noble metals such as Pd, Pt or Au (0.5 wt%).

b) the use/study of heterogeneous catalytic systems for liquid phase selective hydrogenation reactions in the presence of molecular hydrogen. The molecules considered as substrates for the hydrogenation reactions were chosen in order to contain different unsaturated groups in their structure. These are included in Scheme II.1.



Scheme II.1. The molecules considered as substrates for hydrogenation reactions



The materials used in this study were characterized using different structural and morphological characterization techniques such as **adsorption-desorption isotherms of N_2 at -196 °C**, X-ray diffraction (**XRD**), thermogravimetric and differential thermal analysis (**TG-DTA**), X-ray photoelectron spectroscopy (**XPS**), attenuated total reflection Fourier transformed infrared (**ATR-FTIR**), **Raman** spectroscopy, **UV-VIS**, transmission electron microscopy (**TEM**), scanning transmission electron microscopy at high-angle annular dark-field) (**STEM-HAADF**), atomic force microscopy (AFM) and inductively coupled plasma - optical emission spectrometry (**ICP-OES**). Also, chemisorption (H_2, CO_2, NH_3) or desorption (H_2, NH_3, 4-NS) measurements at programmed temperature were performed.

The catalytic tests were performed in a 20 mL stainless steel autoclave, using various solvents such as heptane, ethanol or water. Studies have been conducted varying the pressure, the temperature and the reaction time. Reaction products were identified by gas chromatography and mass spectrometry.

CHAPTER III

Selective hydrogenation of nitroderivatives catalyzed by graphene obtained by the pyrolysis of alginic acid

The synthesis of catalytic materials using alternative preparation methods and the use of precursors from renewable resources is a solution for sustainability. Thus, the processes can be developed in order to provide a viable alternative to the use of inorganic, depleting materials.

The concept of carbocatalysis largely meets all these requirements. From the category of carbon-based materials, graphenes were successfully imposed due to their morphology, to their specific structure, due to the adsorption capacity correlated with the density of the free electrons, and the presence of potentially catalytic active centers (Figure III.1).

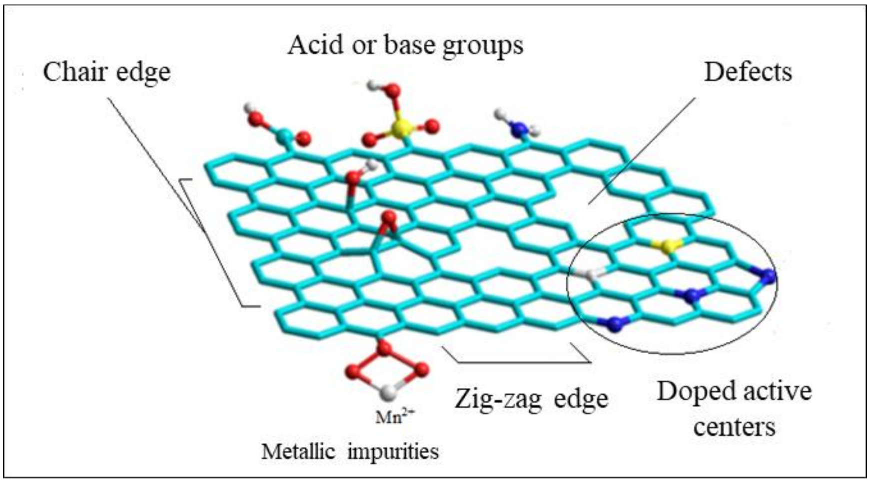
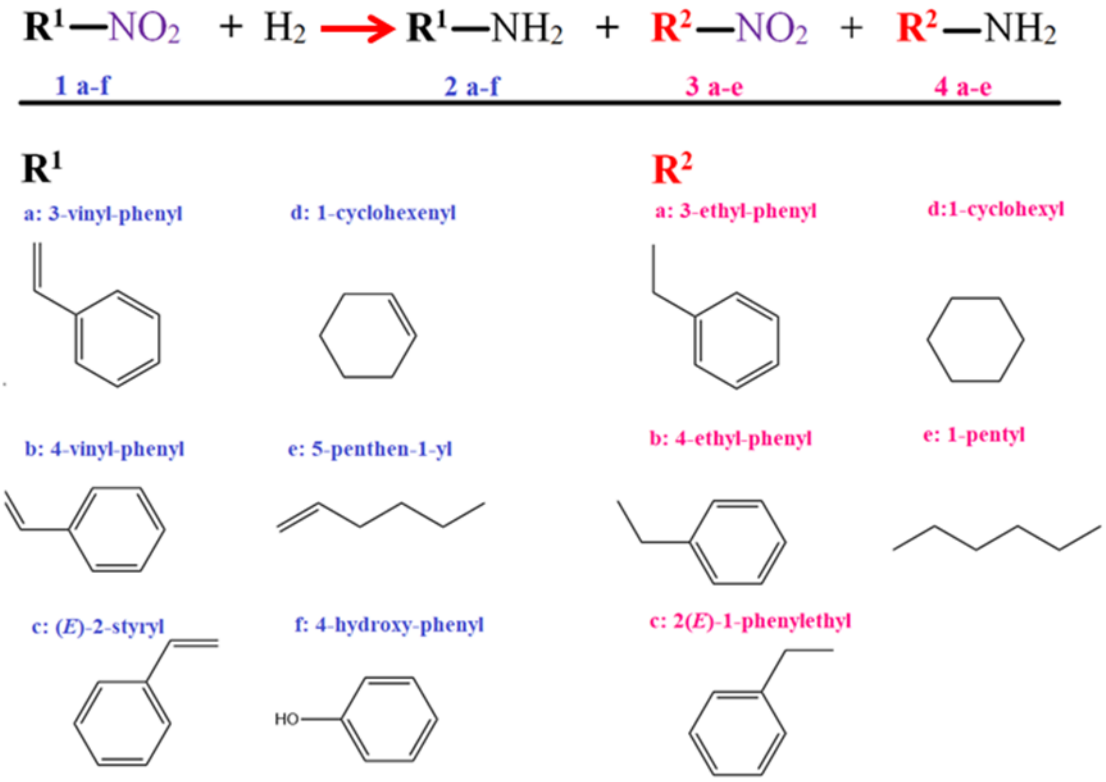


Figure III.1. Catalytic active centers present in graphene[15]

In this chapter it was demonstrated that the graphene obtained by the pyrolysis of the natural alginate, followed by the subsequent exfoliation of the turbostratic graphite residue, unmodified with noble metal, is able to hydrogenate different substrates (see Scheme III.1), even if the process takes place at higher temperatures and the conversions are not very high (see Table III.1). Also, graphene promotes mainly the hydrogenation of nitro groups. Hydrogenation of nitro groups competes with the hydrogenation of the carbon-carbon double bond, and when both functional groups are contained in the molecule, simultaneous hydrogenation can occur.



Scheme III.1. Hydrogenation reaction of the selected compounds (1 a-f)

The nitroaromatic groups or the aliphatic nitro groups are hydrogenated in the presence of the carbocatalyst, without metal in the structure and the reactivity depends only on the nature of the substrate. The performed experiments showed greater reactivity for nitro groups from aliphatic substrates than those derived from aromatic compounds.

Mechanistic research has suggested that the active sites responsible for these hydrogenation reactions are associated with frustrated Lewis acid–base pairs. The performance of the graphene catalysts in these reactions is in a relationship of direct proportionality with the density of these centers.

Overall, this study illustrates the potential of graphenes as carbocatalysts and supports for the hydrogenation reactions.

Table III.1. Results of the hydrogenation of nitro compounds using graphene as metal-free catalyst at 24 h reaction time[a]

Substrate	**Temp.**	**Conversion[b]**	**Selectivity[b]**			**TOF[c]**
	(°C)	**(%)**	**2**	**3**	**4**	**(h^{-1})**
1a	180	**0**	0	0	0	0
1b	140[d]	**14**	65	0	35	3.88
	160	**16**	30	0	70	4.36
	140[e]	**100**	0	0	100	27.88
	140[f]	**0**	0	0	0	0
	140[g]	**11**	42	0	58	3.04
1c	120	**10**	0	0	100	2.76
	160	**42**	0	0	100	11.72
1d	160	**86**	23	63	14	24.00
	160[f]	**9**	29	62	15	2.52
	160[g]	**65**	61	37	6	18.12
	160[h]	**82**	22	63	15	22.77
1e	160	**60**	23	0	76	16.72
1f	180	**8**	100[i]	-	-	2.2

[a] 0.134 mmol substrate, 10 mg catalyst, 5 mL heptane, 30 bar H_2. [b] Conversion of nitro compound and selectivity to the corresponding compounds was determined by GC. [c] Calculated for a reaction time of 6 h taking into account the number of acid sites as determined by NH_3 chemisorption/TPD. [d] 39h reaction time. [e] Using palladium/graphene as catalyst. [f] Adding 134 mmol of acetic acid. [g] Adding 134 mmol of ethyl acetate. [h] Third reaction cycle, 10 mg of graphene reused from first reaction, 0.134 mmol 1d, 5 mL heptane. [i] Selectivity towards 4-aminophenol.

CHAPTER IV

Covalent Organic Frameworks (COF) derived from adamantane - catalysts and supports for Pd or Au in the selective hydrogenation reaction of 4-nitrostyrene

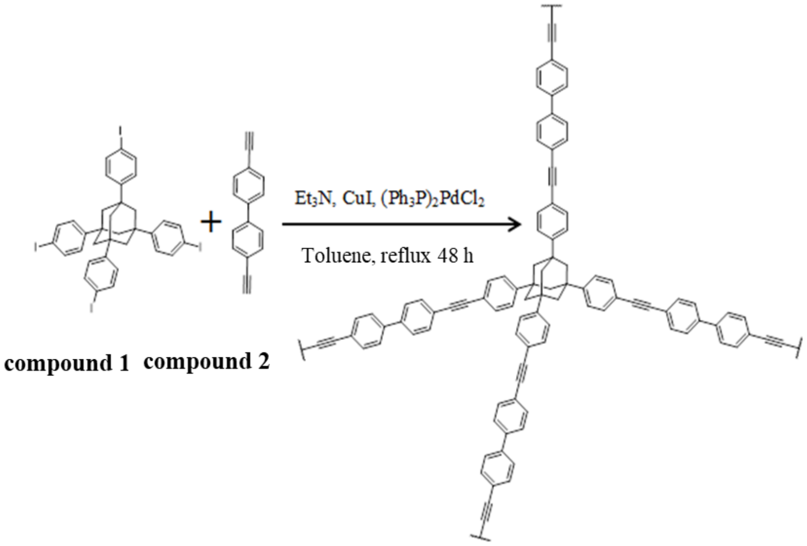
In this chapter, organic covalent frameworks derived from adamantane were used as catalysts and supports for Pd or Au, in the selective hydrogenation reaction of 4-nitrostyrene.

The objective of this chapter was to selectively hydrogenate the C=C double bond in the presence of other reducible groups such as NO_2 from 4-nitrostyrene (4-NS). To achieve the objective, Au or Pd (0.5 wt%) catalysts were employed, using COF polymer as support.

The organic polymer COF was synthesized in the group led by Prof. Ion Grosu, Department of Organic Chemistry at Babeş-Bolyai University, Cluj. The monomer was synthesized by the Sonogashira cross-coupling reaction, starting from the two precursors, **compound 1** and **compound 2** (see Figure IV.1) in the presence of a Pd homogeneous catalyst. Moreover, due to the use of the Pd catalyst in synthesis, it is important to note that the polymer contains remaining Pd from the Sonogashira synthesis (about 0.1 wt%). The obtained material possesses the following properties: i) is a porous polymer with an SSA of 772 m^2/g and bimodal pore distribution; ii) is thermally stable up to 300 °C; iii) the materials is amorphous, as evidenced by X-ray diffraction.

The synthesis of Au/COF and Pd/COF was performed in our laboratory by the precipitation deposition method. Precipitation was accomplished by dropwise addition of a 0.2M solution of NaOH over the metal precursor solution in methanol. The solid obtained was filtered, washed and dried, and part of the material was reduced in H_2 stream at 150 °C during 3h. The materials thus obtained were further characterized. In order to investigate the influence of the catalytic support, Pd/C and Au/C catalysts were synthesized, using the same protocol as for Pd and Au deposited on COF, respectively.

Adsorption-desorption isotherms of N_2 at -196 °C indicate that the texture of the material is retained by the deposition of noble metal. SSA decreases slightly, but this variation may be negligible, demonstrating that the catalytic active phase is evenly dispersed.



compound 1 **compound 2**

compound 3

Figure IV.1. Sonogashira cross-coupling protocol used for the synthesis of COF

X-ray photoelectron spectroscopy (Figure IV.2) highlighted the presence of noble metals on the surface. For Au/COF unreduced material, the presence of Au^{3+} species is observed, whereas the Au^{+} and $Au^{\delta+}$ species are observed after the reduction step. Also, by this technique, the presence of the remnant Pd from the Sonogashira synthesis, was evidenced.

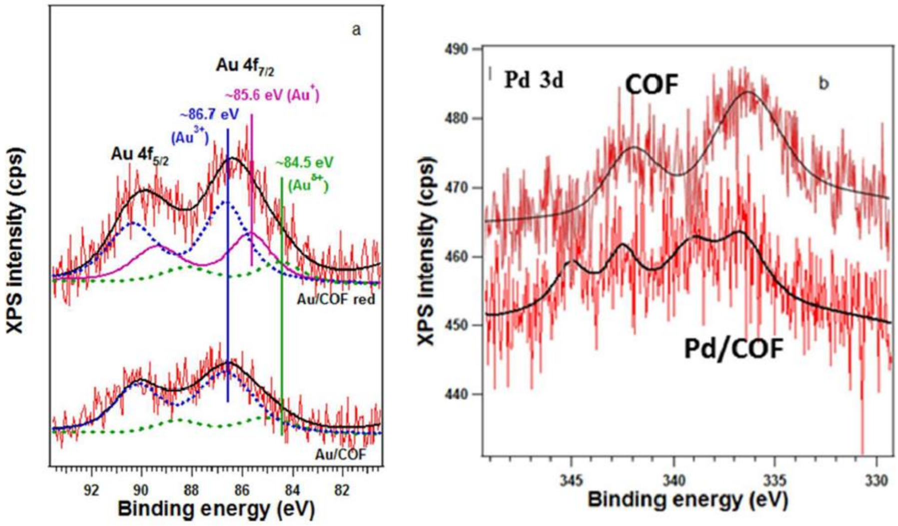


Figure IV.2. XP spectra of reduced and unreduced Au/COF in the region 4f (a) and of Pd/COF and COF in the region 3d (b).

X-ray diffractograms (see Figure IV.3) for Au/COF and Pd/COF indicate that the structure of the polymer is not affected by the deposition-precipitation step. The presence of the remnant Pd from the Sonogashira synthesis, was also evidenced, which is in good agreement with the XP spectroscopy.

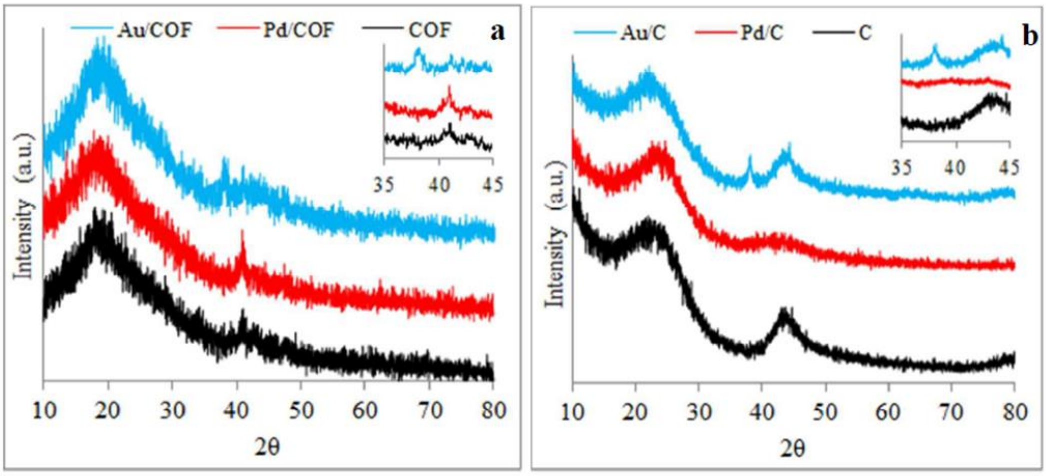


Figure IV.3. XRD patterns of the COF, Pd/COF and Au/COF catalysts (a) and C, Pd/C and Au/C catalysts (b).

The images obtained from the transmission electron microscopy (Figure IV.4) indicate the following: the COF polymer resulted as homogeneous spherical particles with a diameter of 1.7 μm and the residual Pd nanoparticles are highly dispersed with sizes smaller than 1 nm. After the deposition of Pd, spherical particles with a diameter of 4.2 nm can be observed. Au/COF have larger particle sizes of about 13 nm.

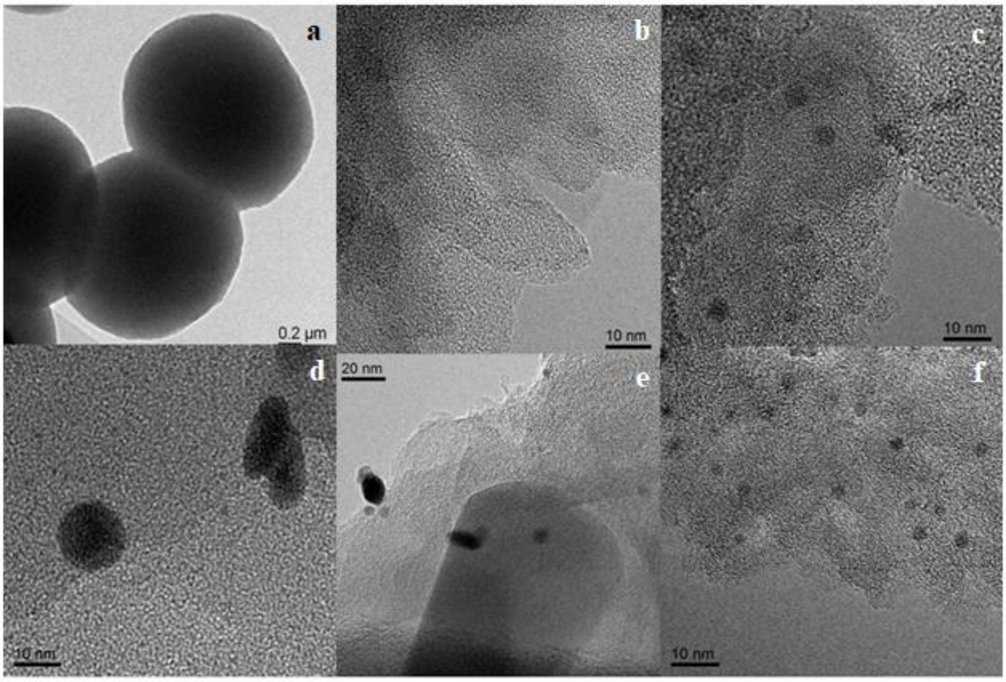
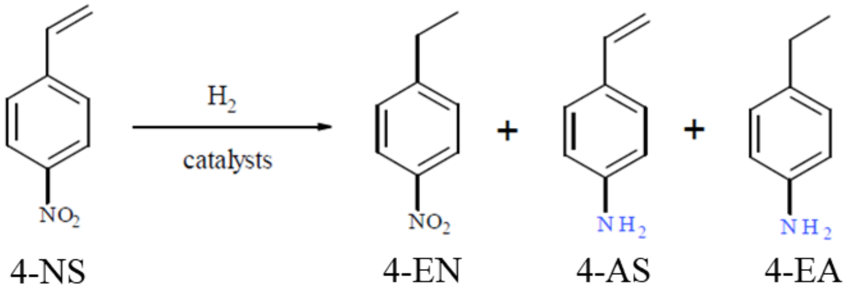


Figure IV.4. TEM of COF (a, b), Pd/COF (c), Au/COF (d), Au/C (e) and Pd/C (f) catalysts.

The catalytic performance of the synthesized materials (COF, Au/COF and Pd/COF) was evaluated in the selective hydrogenation reaction of 4-NS (see Scheme IV.1). The main identified reaction products were 4-ethylnitrobenzene (4-EN), 4-aminostirene (4-AS) and 4-ethylaniline (4-EA). The catalytic tests performed are shown in Table IV.1.



Scheme IV.1. Hydrogenation products for the selective hydrogenation of 4-nitrostyrene

Table IV.1. 4-Nitrostyrene hydrogenation in the presence of COF, Pd/COF, Pd/C, Au/COF and Au/C catalysts

Nr.crt.	Catalyst	Temp. (°C)	Time (h)	Conversion (%)	Selectivity (%)		
					4-EN	4-AS	4-EA
1	-	140	24	0	-	-	-
2	COF	90	6	0	-	-	-
3	COF	140	6	20	100	-	-
4	0.5%Pd/COF	90	0.16	8.6	100	-	-
5	0.5%Pd/COF	90	0.5	74	100	-	-
6	0.5%Pd/COF	90	1	100	100	-	-
7	0.5%Pd/COF	90	24	100	100	-	-
8	0.5%Pd/COF	140	1	100	100	-	-
9	0.5%Pd/COF	140	6	100	97	-	3
10	0.5%Pd/C	90	0.16	85	25	-	75
11	0.5%Pd/C	90	0.5	100	-	-	100
12	Au/COF	90	6	0	-	-	-
13	Au/COF	140	6	20	100	-	-
14	Au/COF red	140	6	60	84	-	16
15	0.5%Au/C	140	6	2	19		81

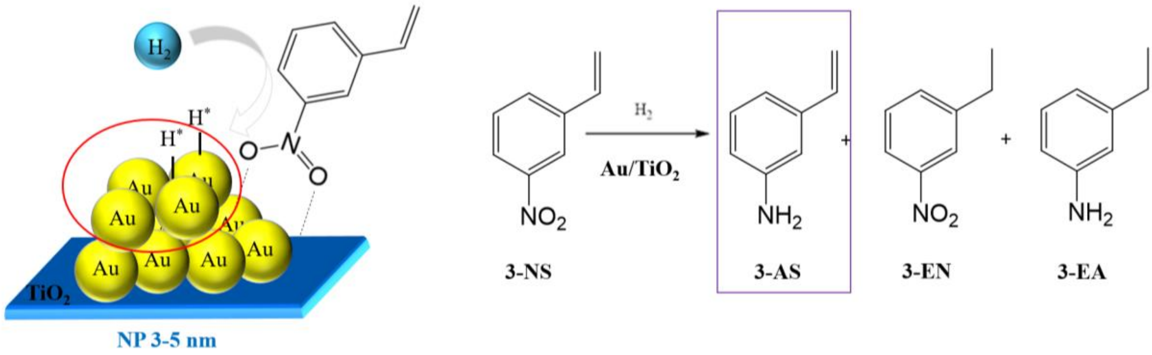
Reaction conditions: 0.067 mmoles of 4-nitrostyrene, 5 mL of heptane, 10 mg of catalyst, 30 atm H_2.

In a first step, the catalyst-free reaction was carried out at 140 ° C for 24 hours to ensure that the homogeneous reaction did not occur (Table IV.1, line 1). Also, the catalytic performance of COF support was evaluated for the 4-NS hydrogenation reaction, in order to see to what extent the remnant Pd influences the catalytic performance. At 90 ° C, the polymer does not hydrogenate the substrate, but at 140 ° C the substrate is hydrogenated with a conversion of 20% (due to the presence of residual Pd) and 100% selectivity at 4-EN, the desired hydrogenation product in this case (see Table IV.1, lines 2, 3). After the supplementary deposition of the additional Pd, the Pd/COF catalyst is much more active, even at 90 °C, retaining the selectivity (Table IV.1, lines 4-9).

The performances of COF polymer as support were compared to active coal. For the same amount of noble metal deposited, Pd/C is much more active, but this material is not selective in the 4-NS hydrogenation reaction (Table IV.1, lines 10, 11).

Au/COF unreduced is not able to hydrogenate the substrate, and by increasing the reaction temperature, it remains inactive (due to the existence of Au^{3+} species, as detected by XPS) (Table IV.1, lines 12, 13). Au/COF_red, however, exhibits catalytic activity in the 4-NS hydrogenation reaction, although it is less active and selective compared to Pd/COF (Table IV.1, line 14).

In the literature,[16, 17] for the case of the hydrogenation reaction of 3-nitrostyrene using Au/TiO_2 catalysts, it has been reported that active sites for H_2 dissociation are low coordinated Au atoms from corners or edges (see Scheme IV.2). For NPs with very small dimensions of 3-5 nm, their concentration is high. In this case, the rate-determining step is the dissociation of the hydrogen on these centers, and the chemisorption of the substrate is preferentially made by the NO_2 group at the metal-support interface; the major hydrogenation product is thus the unsaturated amine (Scheme IV.2).

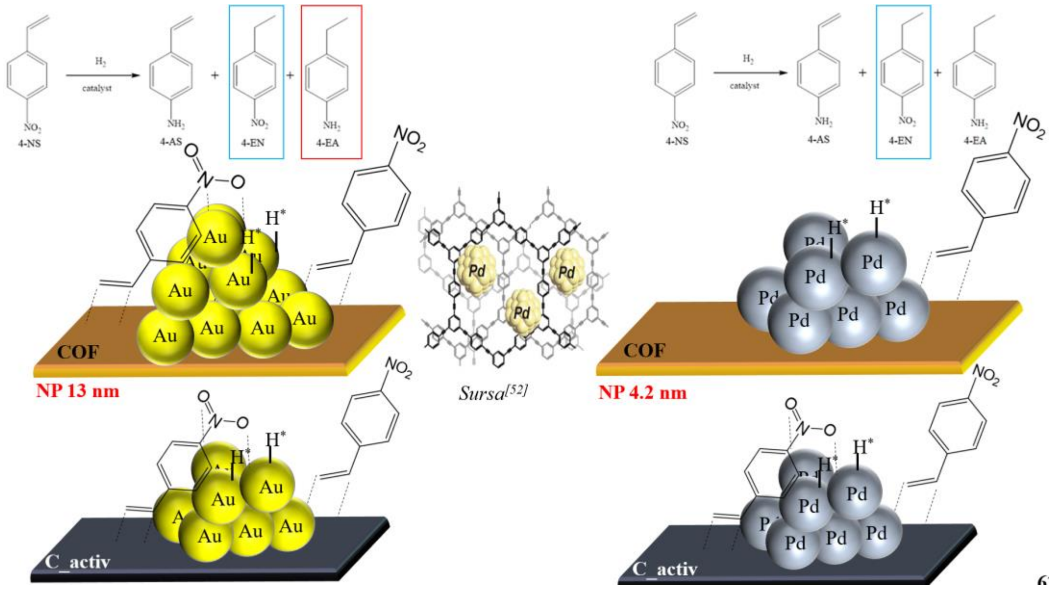


Scheme IV.2. H_2 dissociation and 3-NS chemisorption mode on Au/TiO_2 catalysts

For Au/COF, Au/C and Pd/COF, Pd/C catalysts, taking into account their catalytic performance in the 4-NS hydrogenation reaction, we can conclude that the nature of the support plays an important role in the substrate chemisorption process (see Scheme IV.3.).

Thus, the deposition of Pd on C generated an active but non-selective catalyst. Instead, the Pd/COF catalyst was 100% selective for the hydrogenation of the C=C bond from 4-NS. This behavior was associated with Pd/COF structure, which is a porous material with NP of Pd inside its cavities (as reported in the literature for other types of polymeric materials[14]). Under these conditions, due to a steric hindrance to the substrate, the substrate is selectively chemisorbed by the vinyl group. The chemisorption of the bulkier nitro group is limited under these conditions (see Scheme IV.3) and consequently the process results in 100% selectivity for 4-EN.

The selectivity of Au/COF catalyst is inferior to the Pd/COF catalyst. This behavior can be associated with larger Au particle sizes compared to Pd, and in these conditions, the 4-NS molecule can adsorb on the active sites with both reducible groups, thus allowing the hydrogenation of both functionalities. The influence of the support on the orientation of the molecule to the surface is proven even in this case by higher selectivity for 4-EN. Au/C activity in the 4-NS hydrogenation reaction is also inferior to that of Pd (Table IV.1, line 15), while the selectivity is similar to that of Pd/C catalyst.



Sursa[52]

Scheme IV.3. Schematic representation of the influence of the support for Au/COF, Au/C and Pd/COF, Pd/C materials on the catalytic performance in the selective hydrogenation reaction of 4-NS.

CHAPTER V

Porous organic polymers (POPs) derived from 3,3',6,6'-tetrasubstituted spirobifluorene. Synthesis, characterization and the study of the catalytic activity in hydrogenation reactions.

To highlight the effect of structure/texture of organic polymers as supports for catalysts in the chemoselective hydrogenation reaction of nitroderivatives, a derived objective of this thesis was that of investigating other types of polymeric networks.

For this purpose, another class of organic polymers, namely porous organic polymers (POP), has been synthesized using monomer units such as the 3,3',6,6'-tetrasubstituted spirobifluorene units. POPs were used as supports for Pd and Pt (0.5 wt%) in order to generate selective and reusable catalysts in the hydrogenation reaction of the various ketones as 4-bromobenzophenone (4-BBP), acetophenone (ACP), 7-nitro-1-tetralone (7N-1T) and 1,2-naphthoquinone (1,2-NQ). Also, a nitroderivative aromatic compound was tested (4-nitrostyrene (4-NS)).

POPs synthesis was also carried out by the team led by Prof. Ion Grosu. This consisted of Sonogashira and acetylenic coupling reactions starting from 3,3',6,6'-tetrasubstituted spirobifluorene units. [18] POP1 was synthesized in the presence of a homogeneous Cu catalyst, while POP2-4 in the presence of a homogeneous Pd catalyst, so it is expected that in this case also there will be some residual Pd. The structures of POP1, POP2, POP3 and POP4 supports are shown in Figure V.1.

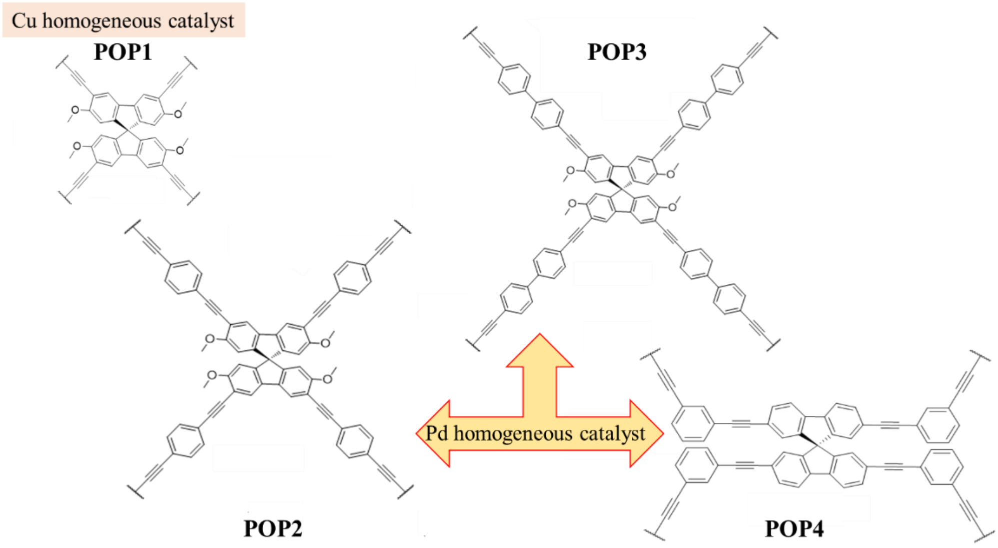


Figure V.1. The structure of POP supports (POP1, POP2, POP3 and POP4)

The synthesized polymers are amorphous materials, thermally stable at temperatures between 200 and 400 °C and exhibit SSA ranging from 300-500 m^2/g, with bimodal pore distribution (see Table V.1).

The specific surface decreases slightly after the noble metal deposition when POP2 polymer is used as a support. However, the pore structure of the support is retained, indicating a good dispersion of the catalytic active phase (Table V.1).

Table V.1. Textural characteristics of the investigated catalysts

Catalyst	SSA BET (m^2/g)	BJH pore size (Å)	SSA Langmuir (m^2/g)	Horwath−Kawazoe pore size (Å)
POP1	377	21, 44	510	8.1
POP2	**583**	**19, 41**	**787**	**8.2**
POP3	271	20, 46	367	8.1
POP4	363	21, 44	492	8.3
Pd/POP2	522	19, 40	704	8.0
Pt/POP2	428	20, 41	587	8.1

The XP spectra (see Figure V.2) revealed the presence on the surface of residual Pd from the POP synthesis. Further Pd deposition revealed the presence of both Pd metal and Pd^{2+} species.

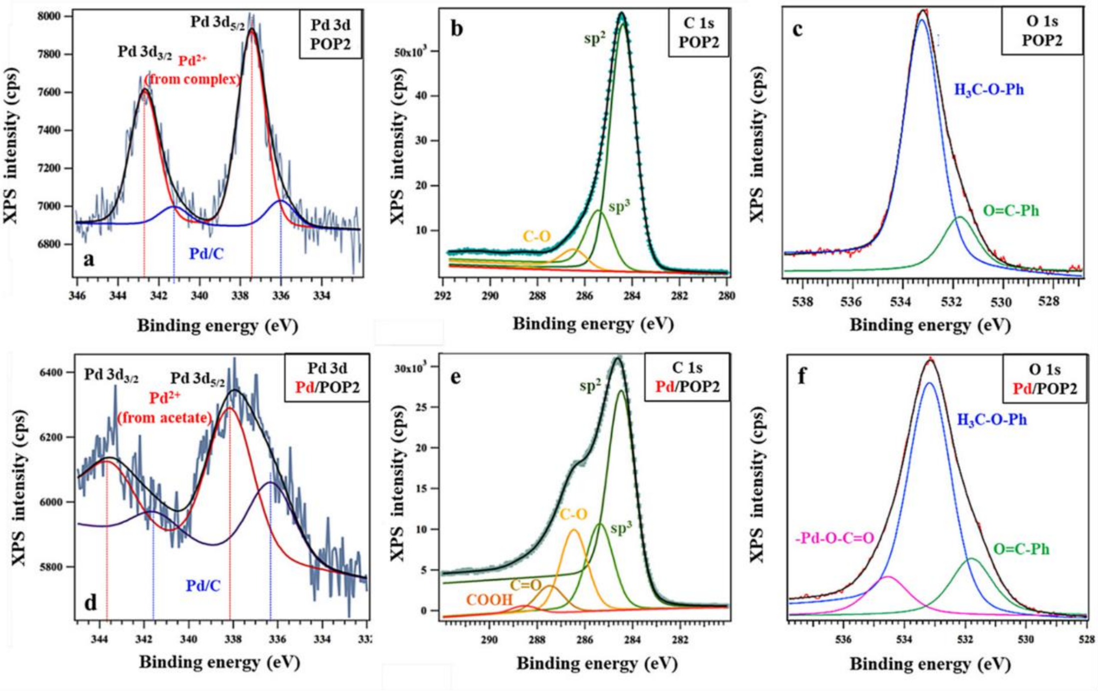


Figure V.2. XP spectra of the Pd3d, C1s and O1s levels for POP2 (a,b,c) and for Pd/POP2 (d,e,f)

The electronic microscopy images describe the morphology of synthesized POP2 material (see Figure V.3a) and confirm the high dispersion of the noble metal after the deposition step (see Figures V.3b-d). In addition, for the Pt/POP$_2$ catalyst (see Figure V.3c and V.3d), the TEM analysis confirms the pore distribution and the results obtained by adsorption-desorption measurements.

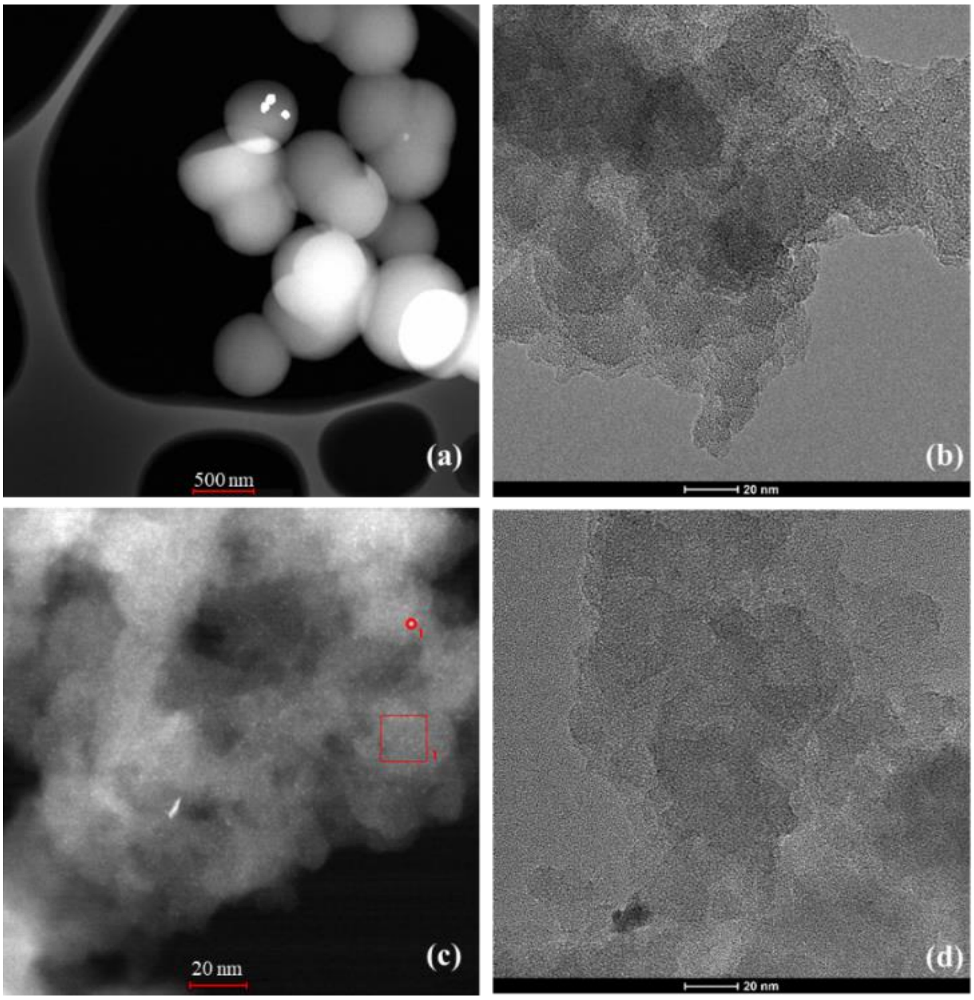


Figure V.3. Electronic microscopy images (a) HAADF, (b) TEM obtained for Pd/POP2 and (c) HAADF, (d) TEM obtained for Pt/POP2.

The catalytic tests performed in the presence of POP1-4 catalysts for the 4-NS hydrogenation show a different conversion of the substrate with 100% selectivity to 4-ethylnitrobenzene (see Table V.2). With the exception of POP1, which was synthesized in the presence of a copper-based catalyst, all other POPs are more active compared to COF, presented in Chapter IV, for the same reaction.[19] Most probably, these results are the consequence of the presence of residual Pd from POPs synthesis, well encapsulated in the polymer framework, which are able to interact with 4-NS.[19]

Table V.2. Catalytic performance of POPs in the hydrogenation reaction of 4-NS

Entry	**Catalyst**	**Time (h)**	**Conversion (%)**	**Selectivity (%)**		
				4-EN	**4-AS**	**4-EA**
1	POP1	6	0.1	100	0	0
2	POP2	6	80	100	0	0
3	POP3	6	45	100	0	0
4	POP4	6	79	100	0	0

Reaction conditions: 0.067 mmoles of 4-NS, 5 mL of heptane, 10 mg of catalyst, 30 atm H_2, temperature 90 °C).

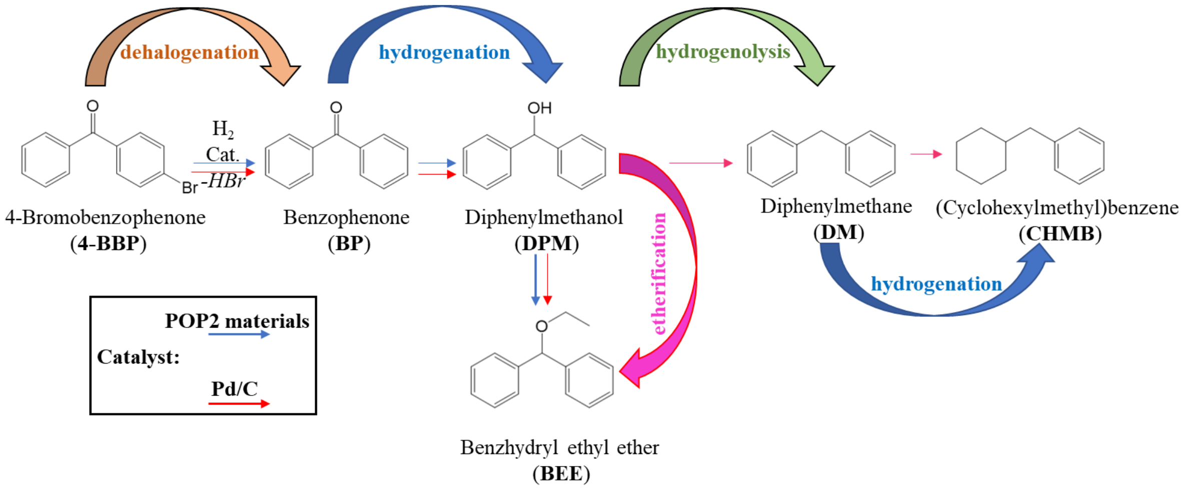
The catalytic performance of POPs was also evaluated in the hydrogenation reaction of various ketones.

For the case of 4-bromobenzophenone, due to residual palladium, the POPs are active in the hydrodehalogenation reaction of the substrate and are very selective for the dehalogenation product, bromobenzophenone (BP). The conversion of the substrate in the presence of different catalysts varied in the order POP4>POP2>POP3 ~ POP1 (Table V.4). Of these, POP2, although to a small extent, was able to further hydrogenate BP to diphenylmethanol (DPM) (selectivity of 7%). Given the structural and textural properties of the POP2 support as well as its catalytic behavior, POP2 was further used as a support in the synthesis of Pd or Pt-containing catalysts.

Additional deposition of noble metal significantly improves the catalytic performance, but the substrate passes a more complex reaction pathway, namely dehalogenation of the substrate followed by the hydrogenation and etherification to benzhydryl ethyl ether (BEE) (see Scheme V.1). The formation of the latter requires the presence of acid catalytic centers, which in this case are represented by the HBr obtained from the hydrodehalogenation reaction. However, the selectivity of the system remains very high for the dehalogenation product.

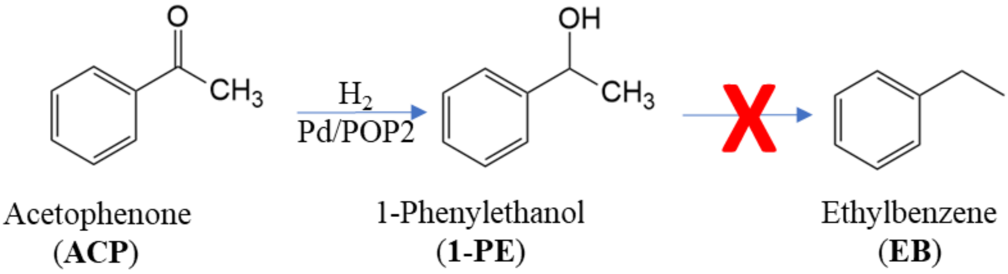
Although Pt/POP2 exhibits almost the same catalytic behavior compared to Pd/POP2 material, for the case of Pt based catalyst, the presence of the DPM hydrogenation compound has been highlighted at higher reaction temperatures, which confirms the proposed reaction pathway for these catalytic systems.

The use of active C as a support for Pd also indicates that this is a less selective material which simultaneously follows two reaction pathways (see Scheme V.1) namely i) hydrodehalogenation/hydrogenation/etherification from 4-BBP to BEE (similar to that followed by Pd/POP2); and ii) hydrodehalogenation/hydrogenation/hydrogenolysis/ hydrogenation from 4-BBP to (cyclohexylmethyl)benzene (CHMB).



Scheme V.1. Reaction pathways and main reaction products obtained in the hydrogenation of 4-BBP.

The catalytic activity of Pd/POP2 was also monitored in the acetophenone (ACP) hydrogenation reaction. In this case, Pd/POP2 is able to hydrogenate the substrate, but the reaction rate is much lower, reaching the total conversion after 30 h. It is important to note that this reaction is 100% selective for 1-phenylethanol (1- PE) (see Scheme V.2), taking into account that Pd-containing materials are generally not selective and also produce the hydrogenolysis reaction with generation of ethylbenzene (EB).



Scheme V.2. Potential products of the hydrogenation of ACP.

The results obtained in the ketones hydrogenation reaction (4-BBP, ACP, 7N-1T and 1,2NQ) on Pd/POP2 and Pt/POP2 catalysts lead to the following conclusions:

✓ In the case of the 4-BBP substrate, in the presence of Pd/POP2 and Pt/POP2 materials, the BP hydrodehalogenation reaction is favored with respect to the hydrogenation reaction of the carbonyl group to 4-bromobenzhydrol. This behavior can be attributed to the electron attracting effects induced in the molecule by the presence of the carbonyl group. These effects lead to a weakening/destabilization of the bond between the Br with the aromatic ring, favoring the dehalogenation reaction. On the other hand, the presence of H* generated by the homolytic dissociation of H_2 may facilitate the dehalogenation reaction of 4-BBP.[20]

The benzophenone is not further hydrogenated to diphenylmethanol in the presence of Pd/POP2 or Pt/POP2 catalysts. This behavior may be due to the competition between HBr generated in the hydrodehalogenation reaction and the more polar behavior of the C=O group. The HBr can block the catalytic active centers and consequently only a small fraction of the molecules (less than 1%) is further hydrogenated and converted to BEE. Another hypothesis is that benzophenone is not further hydrogenated to diphenylmethanol due to a steric hindrance generated by the presence of the second phenyl group in the molecule.[21]

- ✓ For the ACP hydrogenation reaction, the reaction rate is low - the total conversion is reached after 30h. This behavior is due to a stronger chemisorption of the substrate and a slower desorption of the reaction product.
- ✓ The activity and selectivity of Pd/POP2 and Pt/POP2 catalysts in the hydrogenation reactions of 7N-1T and 1,2NQ depend only on the chemical structure of the investigated molecules.
- ✓ The Pd/POP2 catalyst exhibits higher selectivity to 7A-αT in the hydrogenation reaction of 7N-1T. Given the structure of the molecule and taking into account the steric hindrances that may influence the chemisorption of the molecule by the carbonyl group, it was expected that hydrogenation would preferentially take place at the nitro group.
- ✓ The hydrogenation of the carbonyl group such as that from 1,2NQ using Pd/POP2 or Pt/POP2 catalysts, requires relatively high reaction temperatures (180 ºC). The process results in small conversions of the substrate (22 and 52%, respectively), indicating that the molecule is more stable under the given reaction conditions compared to the other ketones.

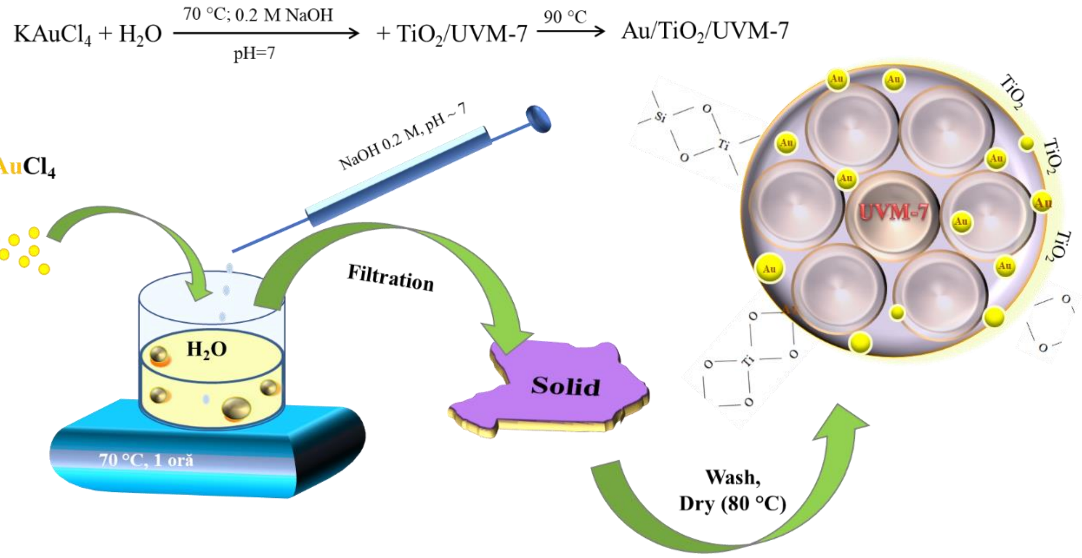
CHAPTER VI.

UVM-7 mesoporous silica - support in the synthesis of Au and/or TiO_2 catalysts - study of the catalytic activity in hydrogenation reactions

This chapter describes another type of mesoporous materials with very high SSA and bimodal pore distribution, as is the case of UVM-7 type silica. This was synthesized for the first time in 2002, in the group led by Prof. Pedro Amoros, at the University of Valencia, Spain.

In this chapter the catalytic performance of UVM-7 type silica materials in the 4-NS selective hydrogenation reaction was studied. The catalysts used in this study were prepared during a research internship at the University of Valencia, Spain.

The synthesis of these materials takes place in three steps: the first step consists in the synthesis of UVM-7 support by the “atran” method[22] starting from triethanolamine and tetraethyl orthosilicate (TEOS), followed by impregnation of the support with TiO_2. The deposition of gold was done by the deposition-precipitation method, which was also used for the other materials and which was described above. Part of the material was also, in this case, reduced in H_2 stream.



$$KAuCl_4 + H_2O \xrightarrow[\text{pH=7}]{\text{70 °C; 0.2 M NaOH}} + TiO_2/UVM\text{-}7 \xrightarrow{\text{90 °C}} Au/TiO_2/UVM\text{-}7$$

Figure VI.1. Schematic representation of the synthesis of the 0.5% $Au/TiO_2/UVM$-7 catalyst.

The materials were then fully characterized. The UVM-7 support has a type IV adsorption-desorption isotherms with two adsorption steps, which confirms the maintenance of bimodal porosity (Figure VI.2 a, b). The SSA of the support is 1091 m^2/g. After the impregnation of the support with 8 wt% TiO_2, the bimodal porosity specific to the UVM-7 type silica is preserved, and the SSA of the material decreases by 18% compared to UVM-7.

Subsequent deposition of gold produces changes in the textural properties of the material. The Au/Ti5/UVM-7 isotherm exhibits a single adsorption step at P/P0>0.5, resulting in the blocking of mesopores formed between nanoparticles, and the SSA decreases by 70%. However, the SSA of the material is still very high and is comparable to the SSA of the previously disclosed polymers.

Increasing the amount of impregnated TiO_2 from 8 to 20 wt%, also affects the textural properties of the UVM-7 support. Ti12/UVM-7 exhibits type IV adsorption-desorption isotherms with an H4 hysteresis associated with irregular narrow pores. As in the case of Au/Ti5/UVM-7, textural changes occur, also, for Au/Ti12/UVM-7 material. The adsorption-desorption isotherms of N_2 at -196 ºC for the synthesized materials and pore distribution are shown in Figure VI.2.

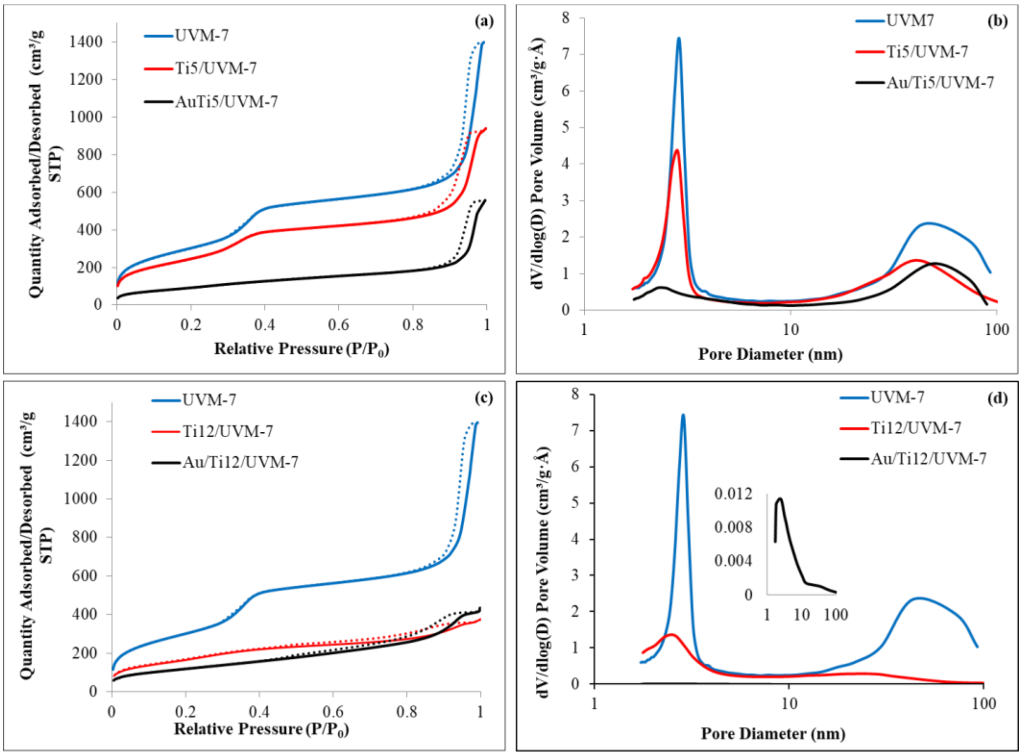


Figure VI. 2. Adsorption-desorption isotherms and BJH pore distribution for SiO_2 based materials (a),(b) impregnated with Au and/or 8 wt.%TiO_2 and (c),(d) impregnated with Au and/or 20 wt%TiO_2.

X-ray diffractograms confirm that the impregnation with TiO_2 or deposition of Au on the surface of UVM-7 does not affect the structure of the material. This behavior suggests the formation of TiO_2 nanodomains, undetectable by XRD.[23] These results also, confirm the high dispersion of Au and TiO_2 on the surface of the silica support.

The diffractograms of the synthesized materials, recorded at small angles, confirm the textural properties of the UVM-7 silica (see Figure VI.3a). UVM-7 shows a intense diffraction line at 2θ~2.2°, corresponding to the (100) reflection of the hexagonal cell unit. It can also be observed that a wider diffraction line at 2θ=4.2°, which is attributed to the overlapping reflections (110) and (200) of the normal hexagonal cell unit (Figure VI.3a).

The intensity and position of the diffraction lines is maintained after impregnation of the support with 8 wt% TiO_2 (Figure VI.3b). After depositing 0.5 wt% Au on Ti5/UVM-7, the diffraction line at 2θ = 2.2° loses the intensity and shifts to lower values of 2θ. This may be a consequence of the partial degradation of the mesoporous material structure after the deposition of gold, and this is also supported by the textural characterization (adsorption-desorption isotherms, TEM).

By further impregnation of the support with 20 wt% TiO_2, the position of the diffraction line corresponding to the reflection (100) of the cell unit is displaced to lower values of 2θ and it disappears completely after the deposition of gold, resulting in degradation of the mesoporous material structure (see Figure VI.3c).

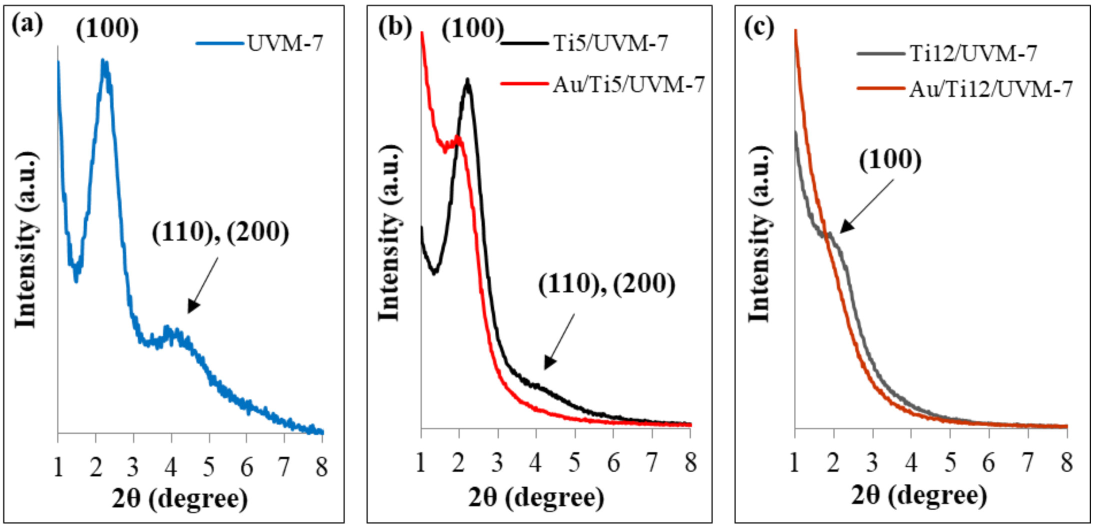


Figure VI.3. X-ray diffractograms at low diffraction angles for a) UVM-7, b) Ti5/UVM-7 and Au/Ti5/UVM-7 and c) Ti12/UVM-7 and Au/Ti12/UVM-7.

XP spectra (see Figure VI.4) highlights presence of Au^+, Au^0 and $Au^{\delta-}$ on the surface, for the unreduced material. As a result of the reduction of the Au/Ti5/UVM-7 sample, some differences in the XPS spectrum were observed; the binding energy at 83.4 eV, corresponding to the Au $4f_{7/2}$ level, suggests the presence of Au^0--$Au^{\delta-}$ interaction. Also, the band at 458.4 eV, corresponding to the Ti $2p_{3/2}$ level, corresponds to the rich electrons Ti species, favoring the interaction between Au and support (TiO_2). [24] In this way, in the unreduced sample there is an electron transfer from TiO_2 to Au, which explains the appearance of the $Au^{\delta-}$ species.

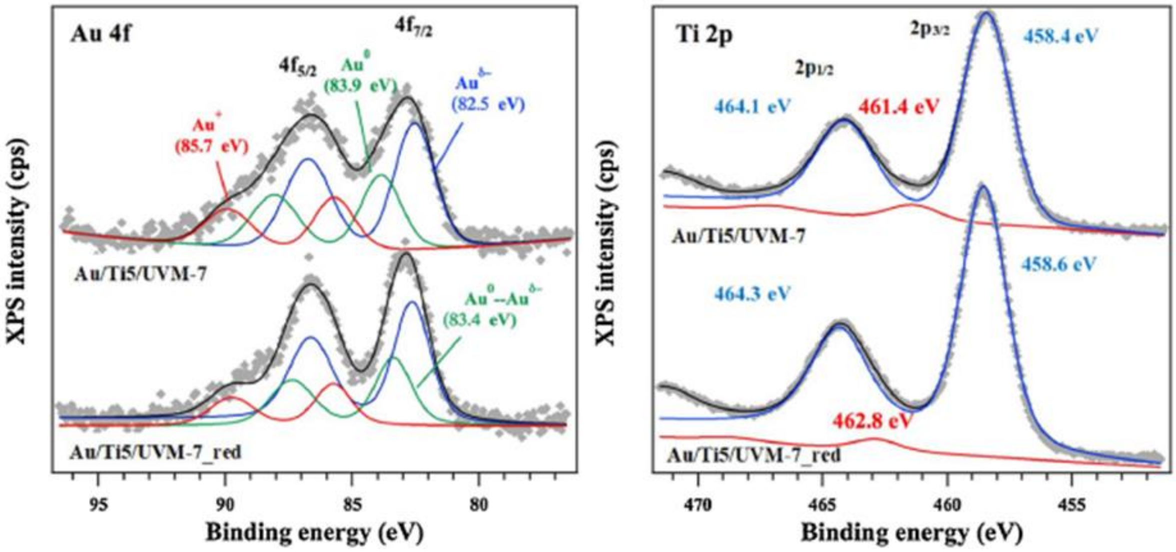


Figure VI.4. XP spectra for Au/Ti5/UVM-7

The images obtained by transmission electron microscopy confirm the bimodal topology specific to the UVM-7 type silica, both in the case of the support and for the Ti5/UVM-7 sample, and demonstrates the alteration of its structure by gold deposition or impregnation with 20 wt% TiO_2. Scanning electron microscopy STEM-HAADF confirm the presence of Au NP for the synthesized materials.

The catalytic performance of the UVM-7 based materials was studied for the 4-NS hydrogenation reaction, and a summary of the catalytic tests performed is shown in Table VI.1.

The catalytic performance of the support in the 4-NS hydrogenation reaction corresponds to a very small, almost negligible conversion (see Table VI.1, line 1). Further deposition of Au on UVM-7 leads to an improvement in catalytic performance (see Table VI.1, line 2), but, as already known from the literature, the metal-support interaction between Au and SiO_2 is poor and Au agglomeration takes place on the surface. In fact, the material is neither selective in 4-NS hydrogenation.

Titanium oxide, however, exhibits a stronger metallic support interaction with Au. This was observed by increasing the catalytic activity in the 4-NS hydrogenation reaction in the presence of Au/TiO_2 catalyst, which, also, has a very good selectivity at 4-AS (see Table VI.1, line 3), as explained, as well, in the previous chapter for Au/TiO_2 systems for 3NS hydrogenation.

Due to the properties of the two types of oxides, Au/TiO_2/UVM-7 has been synthesized in order to combine/benefit from the properties of both SiO_2 for texture and very high SSA and TiO_2 for Au NP stabilization. This was beneficial for the catalytic activity, since the conversion increased to 30% (see Table VI.1, line 4) for the same reaction conditions. The selectivity is very high for the AS, and the total hydrogenation of the molecule may be due to the existence of some larger Au NPs.

The reduced catalyst is less active compared to the unreduced material. This is a consequence of the existence of $Au^{\delta-}$ species in the case of the unreduced material, which means a charge transfer from the support to Au, therefore a higher density of electrons, thus favoring the dissociation of H_2.

Table VI.1. The catalytic performance of the studied materials in the hydrogenation of 4-NS

Entry	**Catalyst**	**Time (h)**	**Conversion (%)**	**Selectivity (%)**		
				AS	**EN**	**EA**
1.	UVM-7	24	**0.1**	100	0	0
2.	Au/UVM-7	24	**2.5**	20	58	22
3.	Au/TiO_2	24	**19**	100	0	0
4.	Au/Ti5/UVM-7	24	**30**	94	0	6
5.	Au/Ti5/UVM-7_red	24	**5**	92	5	3

Reaction conditions: 0.067 mmol of 4-NS, 10 mg of catalyst, 5 mL of heptane, 140 °C, 25 atm H_2 pressure, 0.5% Au on the support.

The limited catalytic performance of this type of materials is due to irreversible adsorption of hydroxylamine on the surface of the catalyst.[25] As reported by Torres et al, [25] the presence of the hydroxyl groups (Si-OH) on the surface of SiO_2 facilitates the interaction with the intermediates formed during the reaction, intermediates which irreversibly adsorb on the surface of the catalyst leading to the blocking of active sites and pores with the main reaction product, 4-AS (see Figure VI. 5).

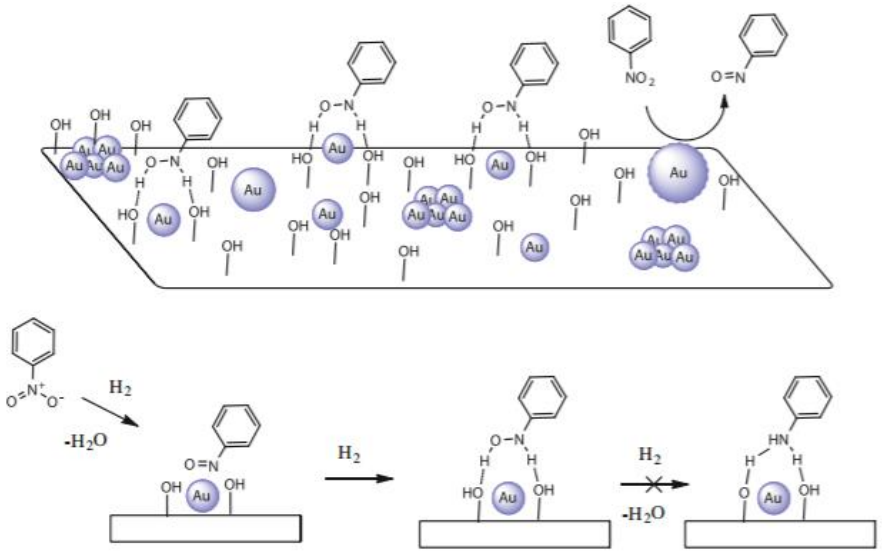
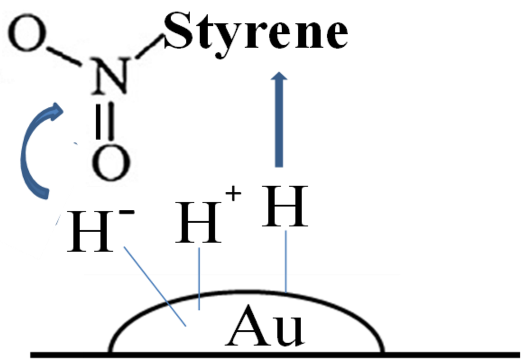


Figure VI.5. Au/SiO_2 catalyst deactivation scheme[25]

According to literature studies, the presence of oxide species dramatically alters the activation of H_2.[26] Thus, metal oxides can permit the heterolytic dissociation of H_2, producing different active species - hydride (H^-) and proton (H^+). Thus, the nucleophilic species (H^-) attacks the nitro group and amine is selectively generated (see Scheme VI.6).

In this way it is explained the high selectivity for the unsaturated amine in the hydrogenation processes of 4-NS or 7N-1T on the Au/Ti5/UVM-7 catalyst (reduced or unreduced), directly related to the heterolytic dissociation of H_2. The H_2 dissociation mechanism proposed in this case is different from that proposed by Corma[17] (described in Chapter IV).



Scheme VI.6. Heterolytic dissociation of H_2 in the presence of metal oxides.

GENERAL CONCLUSIONS

The thesis aimed the synthesis and the study of catalysts based on **new active and selective porous supports** in hydrogenation reactions and the **study of the relations** between the **catalyst structure** and its **selectivity** for a particular reaction product. The materials selected for this purpose were carbon-based materials as i) graphene, active carbon, ii) covalent organic frameworks (COF), iii) porous organic polymers (POPs) and iv) mesoporous materials containing UVM-7 type silica. The deposition of metals on these supports was carried out using conventional synthesis methods (wet impregnation, deposition-precipitation, co-precipitation). The use of these materials pursued several research directions: i) the generation of high SSA supports/catalysts, ii) the control of dispersion and stability of the catalytic active phase on the support, and iii) the evaluation of the metal-support interaction. The materials were used as such in the reaction or as catalytic supports for noble metals such as Pd, Pt or Au (0.5 wt%). The molecules considered as substrates for hydrogenation reactions were selected mostly from aromatic nitroderivatives or aromatic ketones. Catalytic selective hydrogenation reactions have been carried out in liquid phase, in heterogeneous systems, in the presence of molecular hydrogen. The evaluation of the metal-support interaction was performed using characterization techniques such as adsorption-desorption isotherms of N_2, XRD, XPS, ATR-FTIR, TEM, STEM-HAADF. This has allowed the correlation of catalytic behavior with the catalyst structure in hydrogenation reactions.

Chapter I presents the literature study defining the concepts used throughout the thesis, the motivation to in order to choose the considered systems and the current state of the art in the field of selective hydrogenation reactions for nitroderivatives and aromatic ketones.

Chapter II presents the materials used in this thesis and describe the experimental part (characterization techniques used and how the catalytic tests were carried out).

Chapter III was dedicated to the catalytic behavior of the graphene (obtained by the pyrolysis of natural alginate) for the selective hydrogenation reaction of aromatic or aliphatic nitroderivatives containing different reducible groups. Catalytic tests have shown that graphene promotes mainly the hydrogenation of nitro groups, and in the case of molecules containing double bonds, the reaction can proceed with total hydrogenation. Also, the experiments performed indicated a higher activity of the graphene for the hydrogenation of nitro groups from aliphatic substrates compared to those derived from aromatic compounds. The study of the reaction mechanisms suggested that the catalytic active centers are frustrated Lewis acid-base pairs, and the efficiency of the graphene is directly proportional to the density of these centers.

Chapter IV provides information on the catalytic performance of COF materials in the selective hydrogenation reaction of 4-nitrostyrene and information on the adsorption capacity of this material. In accordance with its high specific surface area and bimodal pore distribution, COF absorbs large amounts of polar gases such as CO_2 but is not effective in adsorbing non-polar gases such as H_2, under normal conditions. The synthesis method used for COF support started from adamantane in the presence of a homogeneous Pd catalyst; it does not allow the complete recovery of Pd, which remains encapsulated in the framework and is very well dispersed, as demonstrated by TEM. Used in the 4-NS hydrogenation reaction, COF was able to hydrogenate part of the substrate due to the residual palladium. Additional deposition of Pd led to a substantial increase of the catalytic performance, allowing total substrate conversion under mild conditions (low reaction times and lower temperatures) with selectivity to the product of interest, 4-ethylnitrobenzene. Au deposition on COF does not improve the catalytic performance compared to that of the support, since gold is oxidized on the surface and does not dissociate the hydrogen molecule. Au/COF becomes active at higher temperatures and only after previous reduction in H_2, but is not as selective as Pd/COF. Using another support for Au or Pd, such as active carbon, completely changes the selectivity of the process, this behavior confirming the relationship between the structure of the material and the support and its selectivity in the process. The results were also correlated with the information obtained from material characterization through different techniques: XRD, TEM, and ICP-OES. All synthesized catalysts were stable and reusable.

Chapter V investigated the performance of the porous organic polymers (POPs) in the hydrogenation reaction of 4-nitrostyrene and various aromatic ketones such as 4-bromobenzophenone, acetophenone, 7-nitro-1-tetralone and 1,2-naphthoquinone. The investigated POPs contain spirobifluorene organic entities, bonded covalently. Studies have shown different behavior in the considered hydrogenation reactions. This behavior is the result of the different assembly mode due to the different synthesis protocol. POP1 (completely inactive) was synthesized in the presence of a homogeneous Cu-based catalyst. POP2-4 were synthesized in the presence of a homogeneous Pd based catalyst and showed activity depending on the availability of substrates to the residual Pd. Another element that differentiated the behavior of POPs was the interaction with the encapsulated metal. These materials showed superior activity in the hydrogenation reaction of 4-nitrostyrene compared to COF, even at lower temperatures. Additional deposition of Pd or Pt (0.5 wt%) led to more active catalysts and more stable in the investigated reactions. The influence of the supports was demonstrated by the different behavior of the Me/POP2 catalysts by comparing them with 0.5 wt% Pd/C. In the hydrogenation reaction of 4-bromobenzophenone the Pd/POP2 and Pt/POP2 catalysts produced dehalogenation/hydrogenation/etherification while on Pd/C, the reaction was more complex, following also the dehalogenation/hydrogenation/hydrogenolysis/hydrogenation reaction pathway. Also, platinum, compared to palladium, interacts differently with these supports. Its deposition leads to larger particles and, consequently, to a different catalytic behavior, reflected by selectivity differences.

Chapter VI investigated the catalytic performances of mesoporous materials based on UVM-7 silica (synthesized by the atran method) in the hydrogenation reaction of 4-nitrostyrene and 7-nitro-1-tetralone. The UVM-7 material was, in this case, support for TiO_2 and/or Au. Catalytic studies in the presence of these materials have demonstrated the ability of gold nanoparticles to selectively hydrogenate 4-nitrostyrene to 4-aminostirene, which was very different from the Au/COF behavior. The different selectivity of these materials is due to the different particle size of the catalytic active phase, in addition to the differences between the nature of the supports; NP de Au less than 4 nm are responsible for this behavior. These results have also demonstrated the importance of TiO_2 as an interface between Au and SiO_2, providing stability and better dispersion of the catalytic active phase. It has also been demonstrated that Ti5/UVM-7 is a better support (in terms of selectivity) for Au compared to commercial TiO_2. Contrary to Au/COF, the Au/Ti5/UVM-7 unreduced catalyst is more active and selective due to a charge transfer from TiO_2 to Au, whereby $Au^{\delta-}$ is generated. When Au/Ti5/UVM-7_reduced is used, the pore blocking occurs during the reaction due to the irreversible adsorption of the hydroxylamine intermediates, which limits the diffusion of the reaction products. The data obtained in the hydrogenation reaction of 7-nitro-1-tetralone in the presence of the Au/Ti5/UVM-7 catalyst indicates that this material is more active and selective compared to Pd/POP2 for the same reaction conditions.

In conclusion, this thesis obtained original results regarding the relations between the catalyst structure and its selectivity in the hydrogenation reactions, for a series of carbon-based materials, modified or not with noble metal. These catalysts showed remarkable activities and selectivities in the hydrogenation of substrates with several reducible functional groups (NO_2, C=C, C=O), very difficult to selectively hydrogenate even by homogeneous catalysis, with particular importance in the field of fine chemistry.

DISSEMINATION

I. Articles

1. Mihaela Mirela Trandafir, Alaina Moragues, Pedro Amorós*, Vasile I. Parvulescu*, Selective hydrogenation of nitroderivatives over Au/TiO_2/UVM-7 composite catalyst, Catalysis Today, (2019), DOI: 10.1016/j.cattod.2019.02.053, ISSN: 0920-5861, **IF 4.667**.

2. Mihaela Mirela Trandafir, Lidia Pop, Niculina D. Hădade, Ioana Hristea, Cristian Mihail Teodorescu, Frank Krumeich, Jeroen .A. van Bokhoven, Ion Grosu*and Vasile I. Parvulescu*, Spirobifluorene-based covalent organic frameworks as efficient porous support for Pd and Pt for the selective hydrogenations, *ChemCatChem*, (**2019**), 11, 538-549, **IF 4.674**.

3. Mihaela Mirela Trandafir, Lidia Pop, Niculina D. Hădade, Mihaela Florea, Florentina Neațu, Cristian Mihail Teodorescu, B. Duraki, Jeroen A. van Bokhoven, Ion Grosu,* Vasile I. Pârvulescu*, Hermenegildo Garcia*, An adamantane-based COF: stability, adsorption capability, and behaviour as a catalyst and support for Pd and Au for the hydrogenation of nitrostyrene, *Catalysis Science & Technology*, (**2016**), 6, 8571–8573, DOI: 10.1039/C6CY90113A, ISSN 2044-4761 (online), **IF 5.773**.

4. **Mihaela Mirela Trandafir**, Mihaela Florea, Florentina Neaţu, Ana Primo, Vasile I. Pârvulescu*, Hermenegildo García*, Graphene from Alginate Pyrolysis as a Metal-Free Catalyst for Hydrogenation of Nitro Compounds, *ChemSusChem*, (**2016**), 9, Issue 13, 1565–1569, DOI: 10.1002/cssc.201600197, ISSN 1864-564X (online), **IF 7.226**.

II. International conferences

1. 13th European Congress on Catalysis (**EUROPACAT 2017**), 27-31 august, Florenţa, Italia, 2017, “Adamantane-based COF – new support for palladium and gold catalysts for the selective hydrogenation of 4-nitrostyrene”, **M.M. Trandafir**, L. Pop, N. D. Hădade, M. Florea, F. Neaţu, C.M. Teodorescu, B. Duraki, J.A. van Bokhoven, I. Grosu*, H. Garcia*, V.I. Pârvulescu*, **Oral presentation** (20 min).

III. Presentations

1. Mihaela M. Trandafir, Mihaela Florea, Florentina Neaţu, Vasile I. Pârvulescu, “Selective hydrogenation of 4-nitrostyrene over noble metals based catalysts supported on covalent-organic frameworks”, Scientific Communications Session, Edition XII, 32, 2016, Faculty of Chemistry, University of Bucharest, Romania. **MICROSIN Special Premium** and **Romanian Society of Chemistry Special Award.**

2. **Mihaela M. Trandafir**, Mihaela Florea, Florentina Neaţu, Vasile I. Pârvulescu, “Carbon in the context of green chemistry – applications in catalysis” (“Carbonul în contextul chimiei verzi – aplicaţii în cataliză”), confference organized by POSDRU 155559, at Cheile Gradiştei, Romania, 20-23 November 2015.

IV. Grants and mobility stages

1. A three months **Erasmus** internship at the Institute of Materials Science of Seville, CSIC-University of Seville, in Seville, Spain, 07 July - 01 October 2016.

The experimental activity consisted of: Synthesis of carbon-based materials (graphene, CNT and CNF) and experimental approaches to investigate the preparation of structured carbon monoliths, their characterization and their application as enhanced catalyst carriers to the intensification of important industrial catalytic processes.

2. A five months grant (08.2016-12.2016) received from the strategic grant **POSDRU/187/1.5/S/155559** Competitive multidisciplinary doctoral research at European level (CdocMD) cofinanced by the European Social Found within the Sectorial Operational Program Human Resources Development 2007 – 2013;

3. **Research stage** at the Institute of Materials Science of Valencia (Institut de Ciència dels Materials (ICMUV)), University of Valencia, Valencia, Spain, 16 November-15 December 2015, financial support obtained from POSDRU 155559 project.

The experimental activity consisted of: Synthesis and characterization of silica-based materials (UVM-7 type) containing with TiO_2 and Au.

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