

Research Article

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Catalytic activities of heterogeneous catalysts obtained by copolymerization of metal-containing 2-(acetoacetoxy)ethyl methacrylate

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Abstract: Among the synthetic strategies commonly used for supporting a metal complex onto an organic polymer in order to obtain an heterogeneous catalyst, a valid choice is to synthesize a metal containing monomer (MCM), which can subsequently be subjected to polymerization with suitable comonomers and crosslinkers, achieving a supported transition metal catalyst as a metal-containing polymer (MCP). In this context, during the last two decades, we explored the use of 2-(acetoacetoxy)ethyl methacrylate (HAAEMA) as a ligand to prepare several MCMs for the relevant MCPs. In this review we summarize and discuss our developments in the studies of the catalytic activity of these “hybrid” catalysts. These catalysts have demonstrated high efficiency and/or excellent selectivity in several kinds of chemical reactions and very often they could be recovered and reused in multiple cycles maintaining their activity and selectivity without suffering from appreciable metal leaching.

Keywords: supported transition metal catalysts; heterogeneous catalysts; metal-containing monomers; metal-containing polymers; reductions; oxidations; C-C bond forming reactions.

Abbreviations

AAEMA⁻ – deprotonated form of 2-(acetoacetoxy)ethyl methacrylate; AIBN – azobisisobutyronitrile (IUPAC name: 2,2'-azobis(2-methylpropionitrile)); BSA – N,O-bis(trimethylsilyl)acetamide; cod – 1,5-cyclooctadiene; CP/MAS NMR – Cross Polarization/Magic Angle Spinning Nuclear Magnetic Resonance; (+)-diop – (S,S)-4,5-bis(diphenylphosphinomethyl)-2,2'-dimethyl-1,3-dioxolane; DCE – 1,2-dichloroethane; DEG – diethylene glycol; DMAA – N,N-dimethylacrylamide; DMF – N,N-dimethylformamide; EGDMA – ethylene glycol dimethacrylate; EMA – ethyl methacrylate; *er* – enantiomeric ratio; MBAA – N,N'-methylenebisacrylamide; HAAEMA – 2-(acetoacetoxy)ethyl methacrylate (IUPAC name: 2-(2-methylprop-2-enoyloxy)ethyl 3-oxobutanoate); (R,S)-JOSIPHOS – (R)-1-[(S_p)-2-(diphenylphosphino)ferrocenyl]ethylidicyclohexylphosphine; MCM – metal-containing monomer; [(R,S)-PPFA – (R)-N,N-dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine; TBAB – tetra-*n*-butyl ammonium bromide; TEM – transmission electron microscopy; THF – tetrahydrofuran; TOF – turnover frequency;

1 Introduction

In the last three decades, a large number of researches have been dealt with the possibility of supporting a metal complex onto an insoluble matrix to obtain a heterogeneous catalyst. The matrixes on which metal complexes can be immobilized are generally inert inorganic materials (typically oxides) or organic polymers but the latter, by choosing a suitable combination of comonomers and crosslinkers, in principle allows to control the flexibility of the catalyst as well as to fine-tune its physical properties (polarity, swellability, morphology,

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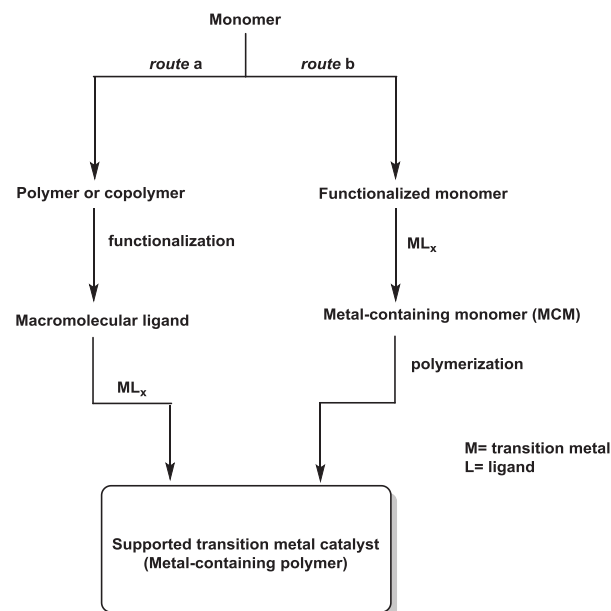
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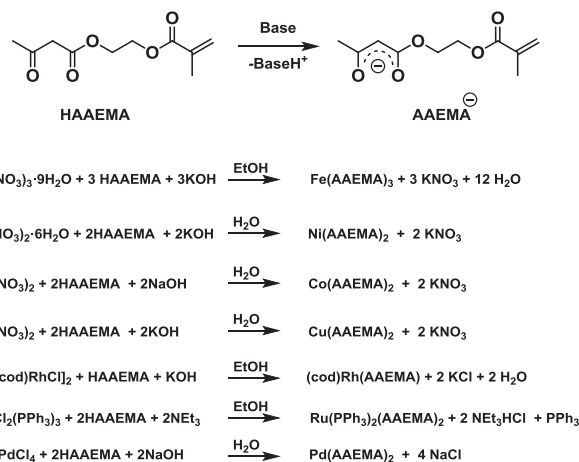
etc.) [1-4]. The only disadvantages of this approach are sometimes the low thermal capacity and mechanical strength of the obtained heterogeneous catalysts [5]. The most commonly used strategies for synthesizing a supported metal complex on organic polymer or resin are essentially those represented in **Scheme 1**.

Route a is the “classic” synthesis of a macromolecular ligand followed by the linking of a transition metal as salt or complex. [2,6] Although the **route b** is less frequently used, it is more interesting both from a synthetic and a catalytic point of view. The **route b** consists of the preparation of a metal containing monomers (MCM), *i.e.* a catalytically active transition metal complex with a ligand having a functionality, which can subsequently be subjected to polymerization with suitable comonomers and crosslinkers for achieving a supported transition metal catalyst as a metal-containing polymer (MCP). Moreover, the use of MCMs offers the advantage of a possible comparison of the activity between the homogeneous and the heterogeneous phase as well as a more uniform distribution of the transition metal in the support with respect to **route a**, and thus a more controllable dispersion of the metal in the polymer matrix. The use of MCMs for the obtainment of heterogeneous catalysts has been reviewed by some of us in the 2004 and more recently in 2013. [7,8] In this framework, during the last two decades, we explored the use of 2-(acetoacetoxy) ethyl methacrylate (HAAEMA) as a ligand to prepare several MCMs for the obtainment of relevant MCPs. HAAEMA (**Scheme 2**) is a clear or light-yellow liquid which finds use as versatile functional acrylic monomer [9-14] for making copolymers to be used in various applications such as, by way of example, dental resins, [15,16] coatings for glass and metal surfaces, [17] wound sealants, [18] waterborne coatings, [19,20] thermal nanoimprint lithography, [21] and nanoparticles [22-25]. On the other hand, exploiting the fact that the reactivity of the β -ketoester functionality in HAAEMA towards transition metal salts or complexes is very close to that of acetylacetone, we were able to prepare several transition metal complexes containing the ligand AAEMA⁻ (**Scheme 2**).

The spectroscopic features of all AAEMA⁻ complexes demonstrate that the β -ketoester moiety is the sole functionality involved in the coordination while the methacrylic tail is indeed left free for other reactions, such as radical polymerizations. Thanks to these characteristics, it was possible to synthesise and employ in catalysis several polymer-supported transition metal catalysts obtained from copolymerization of transition metal-containing AAEMA⁻ with appropriate comonomers and crosslinkers (**Scheme 3**). All resulting MCPs are non-hygroscopic powders which are insoluble in all solvents

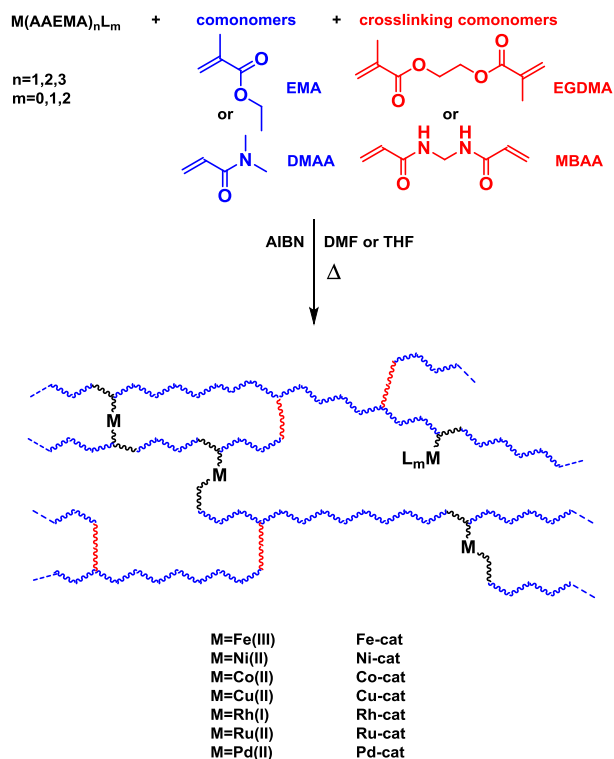


Scheme 1:



Scheme 2:

but they swelled well in water, acetone, halogenated solvents, dioxane, THF, DMF, and shrink when treated with diethyl ether, ethyl acetate or petroleum ethers. These swellabilities are very valuable in looking for new catalytic systems that could be recoverable and recyclable. In this review, we summarize and discuss our developments in the studies of catalytic activity of these “hybrid” catalysts. We will focus on their advantages in terms of recyclability without forgetting to point out some of their drawbacks. The discussion on the various MCPs has been subdivided into paragraphs each of which dealing with a single transition metal.



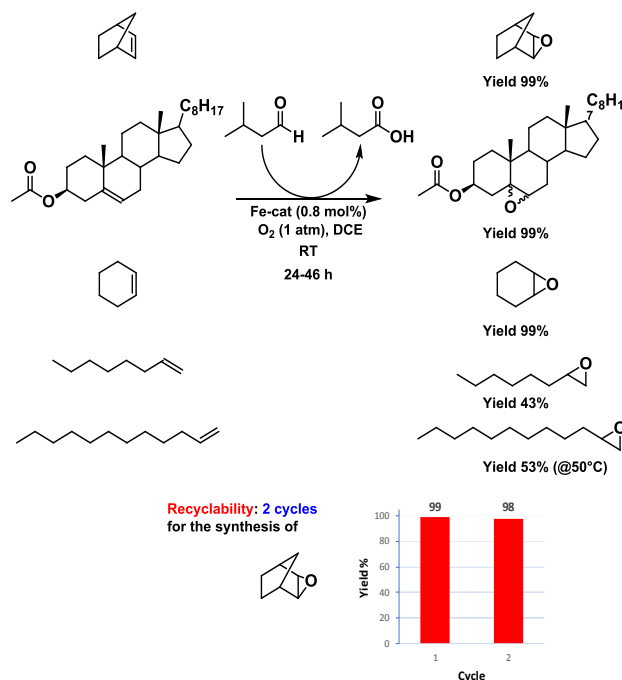
Scheme 3:

2 Catalytic activity of Fe-cat

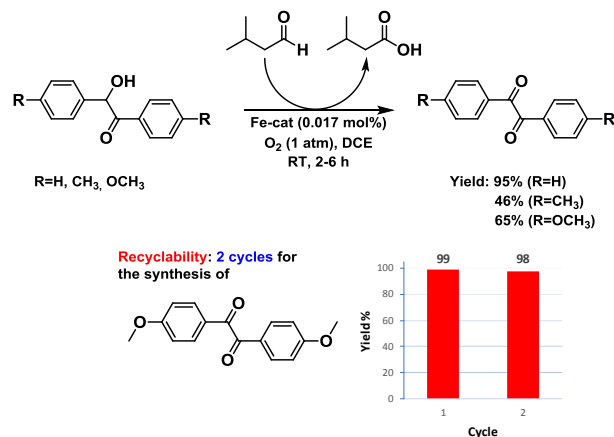
Fe-cat was obtained as orange solid by copolymerizing the complex $\text{Fe}(\text{AAEMA})_3$ with DMAA as comonomer, and MBAA as crosslinker in DMF at 50°C for 24 h (**Scheme 3**) [26]. The first application of **Fe-cat** was in the catalytic aerobic epoxidation of olefins (**Scheme 4**) in presence of isovaleraldehyde as coreductant at room temperature in 1,2-dichloroethane (DCE). Under these reaction conditions, also known as “Mukaiyama’s conditions”, [27] **Fe-cat** proved to be highly active and selective for the epoxidation of unsaturated substrates such as norbornene, cholesteryl acetate, and cyclohexene. The catalytic system was recyclable without loss of activity except for the epoxidation of open chain alkenes such as 1-octene and 1-dodecene where **Fe-cat** suffered from a severe metal leaching.

Under “Mukaiyama’s conditions”, **Fe-cat** was also used as heterogeneous catalyst for the aerobic oxidation of α -hydroxyketones to α -diketones (**Scheme 5**) [28].

With a very low amount of catalyst, substrates such as benzoin, 4,4'-dimethyl-benzoin, and anisoin were smoothly oxidized to corresponding α -diketones in moderate to good yield, and **Fe-cat** was easily separable from the reaction mixture and recyclable at least once without suffering from metal leaching.



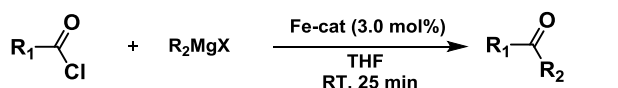
Scheme 4:



Scheme 5:

Finally, **Fe-cat** also catalysed a carbon–carbon bond-forming reaction such as the cross-coupling between acyl chlorides and Grignard reagents, [29] affording several aliphatic or aromatic ketones in moderate to excellent yield (**Scheme 6**).

At least in one instance, it was possible to recycle **Fe-cat**, which showed a comparable activity and selectivity with respect to the first cycle.



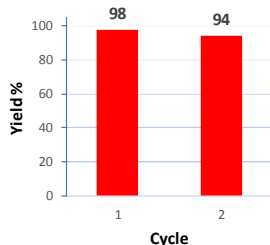
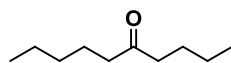
$R_1 = n\text{-C}_5\text{H}_{11}, \text{Ph}$

$R_2 = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9, n\text{-C}_9\text{H}_{19}, \text{Ph}, \text{C}_6\text{H}_4\text{-}p\text{-OCH}_3$

$X = \text{Cl}, \text{Br}$

12 examples
Yields: 42-98%

Recyclability: 2 cycles for the synthesis of



Scheme 6:

3 Catalytic activity of Ni-cat

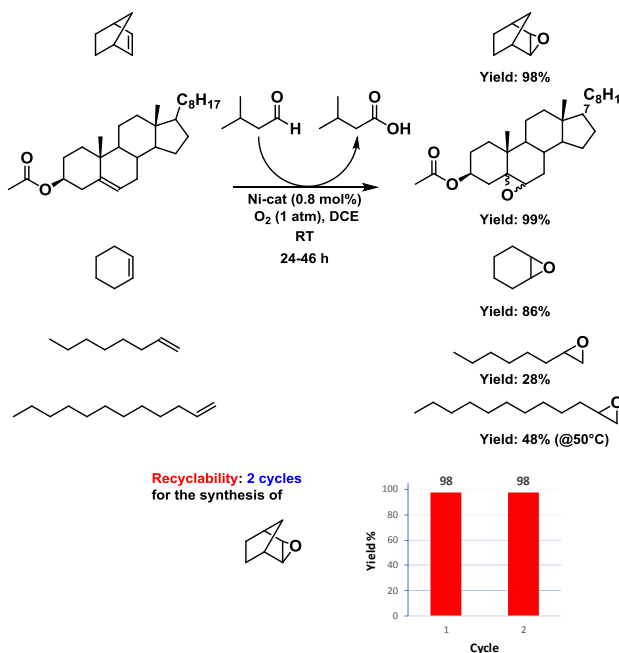
Ni-cat was obtained as pale green powder by copolymerizing the complex $\text{Ni}(\text{AAEMA})_2$ with DMAA as comonomer, and MBAA as crosslinker in DMF at 120°C for 24 h (Scheme 3) [26].

The first application of **Ni-cat** in catalysis was the aerobic epoxidation of olefins under “Mukaiyama’s conditions” and, like **Fe-cat**, **Ni-cat** proved to be active, selective, and recyclable for the epoxidation of norbornene, cholesteryl acetate, and cyclohexene. In the epoxidation of linear alkenes also this catalyst suffered from a severe metal leaching (Scheme 7).

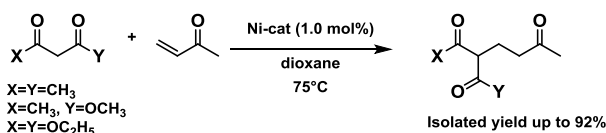
The **Ni-cat** was also used as heterogeneous catalysts for Michael addition reactions (Scheme 8) [30].

When the Michael donor was methyl acetoacetate ($X=\text{CH}_3$; $Y=\text{OCH}_3$), the best yield (92%) of the relevant adduct was achieved within 19 h. The recycle test gave 76% yield after 24 h. This case represents the best compromise in terms of activity and metal leaching (20% of initial amount) of **Ni-cat**. For other donors, the adduct yields were lower and metal leaching for **Ni-cat** was even more significant (up to 87% of initial amount).

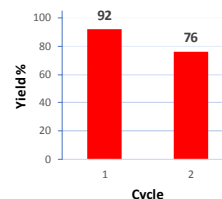
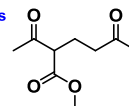
More recently, we explored the use of **Ni-cat** for accelerating the transfer hydrogenation of nitroarenes in aqueous media using NaBH_4 as the reducing agent. Although preliminary catalytic tests using nitrobenzene as the representative substrate were encouraging (isolate yield up to 93%), attempts to recycle **Ni-cat** failed. In the second run, the yield into aniline dropped to 27% due to severe metal leaching. Nevertheless, we found that by submitting **Ni-cat** to thermal annealing at 300°C



Scheme 7:



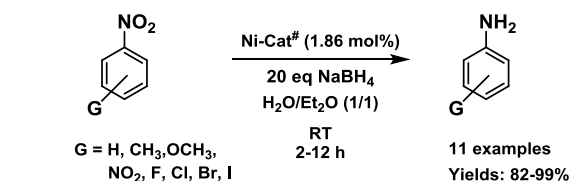
Recyclability: 2 cycles for the synthesis of



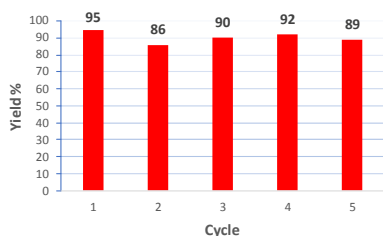
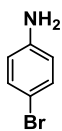
Scheme 8:

under nitrogen a polymer supported nickel nanomaterial (**Ni-cat**[#]) was formed which proved to be a very active and selective catalyst for the hydrogenation of several functionalized nitroarenes to corresponding aromatic amines in aqueous medium at room temperature in the presence of NaBH_4 (Scheme 9) [31].

Remarkably, **Ni-cat**[#] was found highly selective in the hydrogenation of halonitrobenzene to haloaniline, avoiding the formation of hydro-dehalogenated side-products, and displayed excellent recyclability for five cycles without suffering from metal leaching.



Recyclability: 5 cycles
for the synthesis of



Scheme 9:

4 Catalytic activity of Co-cat

Co-cat was obtained as pink solid by copolymerizing the complex $\text{Co}(\text{AAEMA})_2$ with DMAA as comonomer, and MBAA as crosslinker in DMF at 50°C for 24 h (Scheme 3) [26]. In the aerobic epoxidation of olefins under “Mukaiyama’s conditions”, like **Fe-cat** and **Ni-cat**, **Co-cat** was active, selective, and recyclable for the epoxidation of norbornene, cholesteryl acetate, and cyclohexene but again a severe metal leaching was observed in the epoxidation of linear alkenes (Scheme 10).

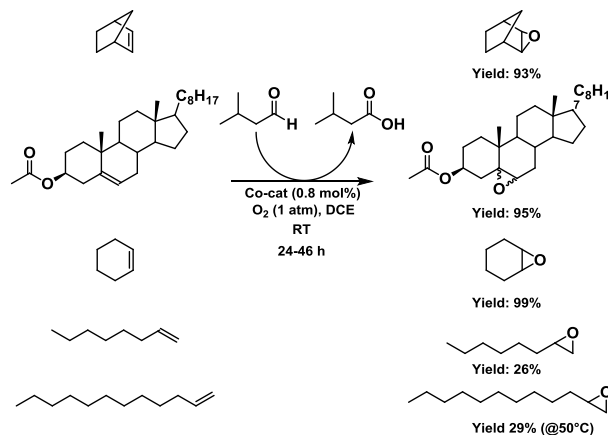
Under “Mukaiyama’s conditions”, **Co-cat** acted as heterogeneous catalyst also for the aerobic oxidation of α -hydroxyketones to α -diketones, displaying a higher activity than **Fe-cat** (Scheme 11) [28].

Benzoin, 4,4'-dimethyl-benzoin, and anisoin were smoothly oxidized to the corresponding α -diketones in good to excellent yields and **Co-cat** was recyclable at least once without appreciable metal leaching.

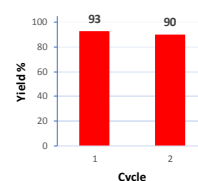
Moreover, **Co-cat** compared to **Fe-cat** and **Ni-cat** demonstrated to be the most versatile catalyst in the oxidation reactions. In fact, **Co-cat** was also an active and recyclable heterogeneous catalyst for the selective oxidation of disubstituted sulfides to sulfoxides and/or sulfones under “Mukaiyama’s conditions” (Scheme 12 and Table 1) [32].

The selective formation of the intermediate sulfoxide was achieved by lowering the partial pressure of the oxidant, using dried air in place of pure dioxygen, and matching with the time reactions.

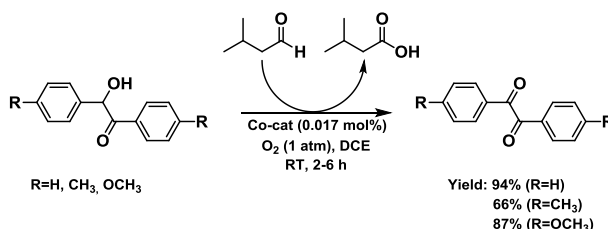
Having optimized the reaction conditions for the obtainment of sulfoxides, the highly regioselective oxidation of a bis-sulfide such as 2-(2-p-tolylsulfanyl-



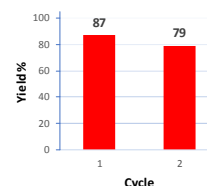
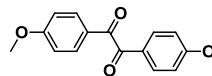
Recyclability: 2 cycles
for the synthesis of



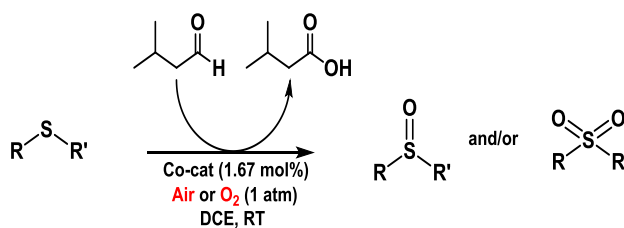
Scheme 10:



Recyclability: 2 cycles for
the synthesis of



Scheme 11:



Scheme 12:

Table 1: Oxidation of disubstituted sulphides catalysed by Co-Cat under Mukaiyama's conditions.

Entry	Substrate	Oxidant	Time (h)	Yield in sulfoxide (%)	Yield in sulfone (%)
1	(CH ₃) ₂ S	Air	8	80	–
2	(CH ₃) ₂ S	Air	20	–	>99
3	(<i>n</i> -Bu) ₂ S	Air	21	83	10
4	(<i>n</i> -Bu) ₂ S	Air	37	8	92
5	(<i>t</i> -Bu) ₂ S	O ₂	3	–	>99
6	(PhCH ₂) ₂ S	O ₂	8	–	>99
7	<i>p</i> -Tol-S-CH ₃	O ₂	2	–	>99

ethylsulfanyl)-benzothiazole into the corresponding sulfoxide 2-[2-(toluene-4-sulfinyl)-ethylsulfanyl]-benzothiazole in 93% yield was successfully obtained (Scheme 13) [33].

Co-cat also acted as an active and reusable catalyst for the oxidation of benzylic and secondary alcohols at 40°C under “Mukaiyama's conditions” (Scheme 14) [34].

The corresponding carbonyl or ketone compounds were achieved in good to excellent yields and **Co-cat** was recycled at least four times without negligible metal leaching.

Pursuing our studies on the aerobic catalytic oxidation of organic substrates, we also found that **Co-cat**, under very mild conditions, behaved as a recyclable heterogeneous catalyst for the oxidation of alkyl and aryl phosphines to the corresponding oxides [35].

The **Co-cat** was an active heterogeneous catalyst for Michael addition reactions (Scheme 15) [30].

As in the case of **Ni-cat**, when the Michael donor was methyl acetoacetate (X=CH₃; Y=OCH₃), the best yield (97%) of the relevant adduct was obtained within 19 h while a 93% yield was obtained in the recycle test after 19h. Although **Co-cat** was a more active catalyst towards Michael reaction with respect to **Ni-cat**, its metal leaching was much higher. For example, in the case of methyl acetoacetate (X=CH₃; Y=OCH₃) it was 65% of initial amount (for **Ni-cat**, it was 20% of initial amount, see above).

5 Catalytic activity of Cu-cat

The supported copper complex **Cu-cat**, was obtained as green solid from copolymerization of Cu(AEMA)₂ with DMAA as comonomer, and MBAA as crosslinker in acetone/DMF (1/1) at 60°C for 5 h (Scheme 3). **Cu-cat** as **Fe-cat** and **Co-cat** was tested as metal catalyst in several

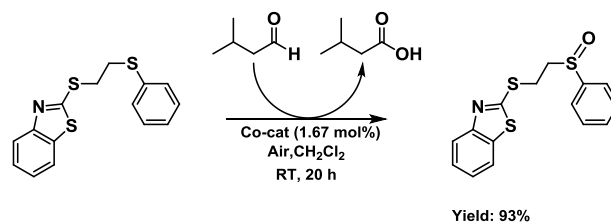
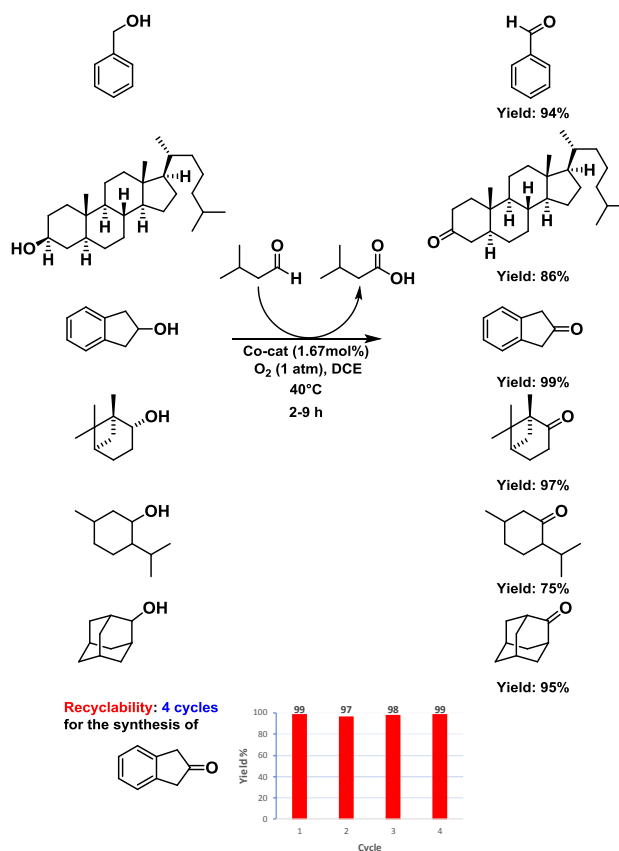
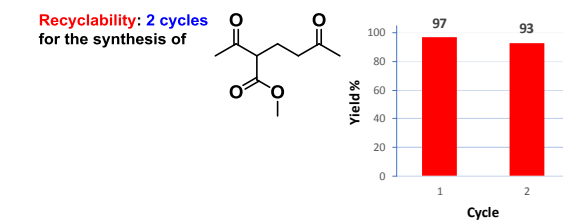
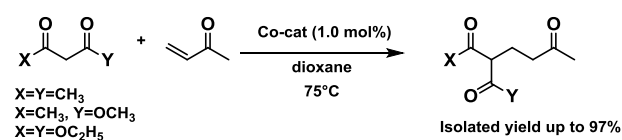
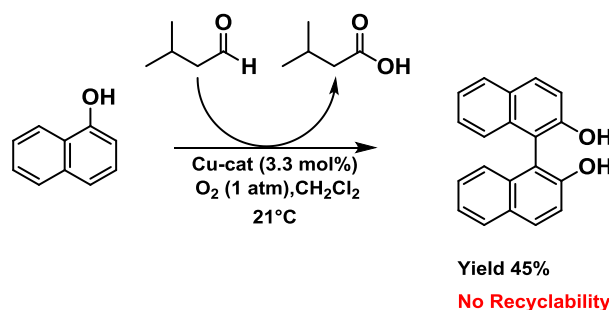
**Scheme 13:****Scheme 14:****Scheme 15:**

Table 2: Hydrogenation of unsaturated substrates catalyzed by **Rh-cat** (0.625 % mol).

Entry	Substrate	solvent	T (°C)	P (bar)	Time (h)	Product	Yield (%)
1	1-heptene	CH ₃ OH	21	1	4	<i>n</i> -heptane	>99
2	cyclohexene	CH ₃ OH	21	1	2	cyclohexane	>99
3	(-)-carvone	CH ₃ OH	21	1	6.5	carvotanacetone	77
4	citral	CH ₂ Cl ₂	21	1	54	citronellal	64
5	cinnamaldehyde	CH ₂ Cl ₂	21	20	8	3-phenylpropanal	68
6	valeronitrile	CH ₃ OH	21	20	6	dipentylamine	85
7	nitrobenzene	CH ₃ OH	50	1	18	aniline	>99

oxidations under Mukaima's condition, but the obtained results were not encouraging with respect to them. On the other hand, **Cu-cat** was an active catalyst (**Scheme 16**) in the oxidative coupling of 2-naphthol for obtaining 1,1'-bi-2-naphthol. However, the yield was moderate, and the catalyst was not recyclable [36].

**Scheme 16:**

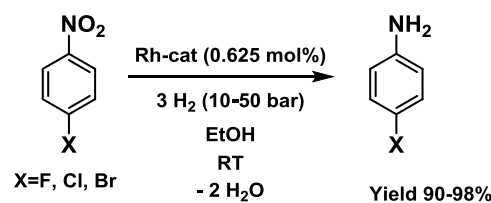
The synthesis of **Rh-cat** (**Scheme 3**) was achieved submitting the complex Rh(cod)AAEMA to copolymerization with DMAA and MBAA at 110°C in DMF in the presence of AIBN as radical initiator, obtaining a greenish-black powder. [37] **Rh-cat** catalysed the hydrogenation of several unsaturated substrates (**Table 2**) in methanol or CH₂Cl₂ with yields ranging from 64 to >99% under very mild conditions.

Only cinnamaldehyde (entry 5), and valeronitrile (entry 6) required higher H₂ pressure (20 bar) for their reduction. Five recycles of **Rh-cat** were made in the case of 1-heptene hydrogenation, without activity loss.

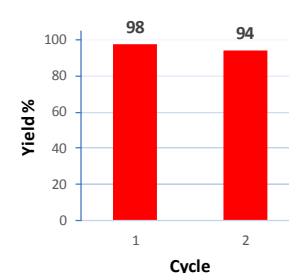
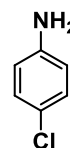
Encouraged by the good results achieved in nitrobenzene reduction (**Table 2**, entry 7), we employed **Rh-cat** in the reduction of *p*-halo-nitrobenzenes into *p*-halo-anilines (**Scheme 17**) [38].

Although the average turnover frequencies (TOF's) of catalysis were very low (from 0.95 up to 7.6 h⁻¹), the selectivities were very high, thus minimizing concurrent hydrodehalogenation. In the recycle tests **Rh-cat** was even more active (average TOF's up to 12.0 h⁻¹) but 6-8% of by-products such as *p*-halonitrosobenzene and 4,4'-dihaloazobenzene was also formed.

A chiral version (**Rh-cat***) of **Rh-cat** was synthesised by exchanging the cod ligand in (cod)Rh(AAEMA) with the (S,S)-DIOP and copolymerizing the resulting complex [(+)-diopRh(AAEMA)] with DMAA and MBAA in presence of AIBN in toluene/DMF at 100°C (**Scheme 18**) [39].



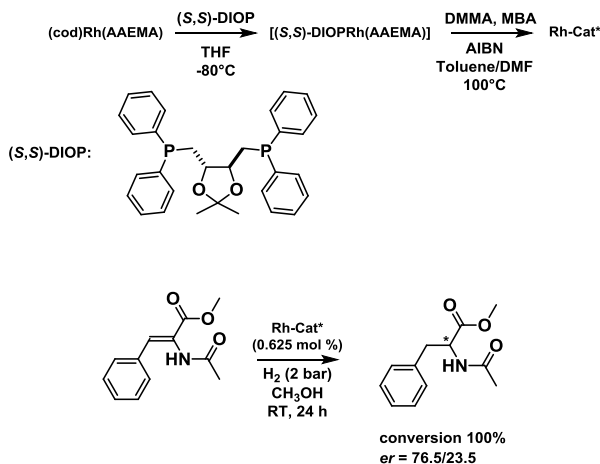
Recyclability: 2 cycles
for the synthesis of

**Scheme 17:**

Rh-cat* accelerated the hydrogenation of methyl-(*Z*)- α -N-acetamidocinnamate to N-acetyl-(*S*)-phenylalanine methyl ester with enantiomeric ratio (*er*) up to 76.5/23.5. However, **Rh-cat*** showed a lower enantioselectivity with respect to the homogeneous counterpart [(*S,S*)-DIOPRh(AAEMA)], which reached *er*=83.5/16.5. Thanks to CP/MAS ³¹P NMR studies [40-42], it was found that the lowering of enantioselectivity is due to the partial

oxidation of the (*S,S*)-DIOP ligand that occurs during the copolymerization of [(*S,S*)-DIOPRh(AAEMA)]. In the recycle test reactions, **Rh-cat*** unfortunately halves its activity, lowering its enantioselectivity (*er* up to 65.0/35.0).

Finally, **Rh-cat** was also found to facilitate carbon-carbon bond forming reactions. In fact, employing it as heterogeneous catalyst for the polymerization of phenylacetylene or *p*-tolylacetylene, polymers with excellent yields and very high stereoregularities were obtained [43]. In this framework, it was ascertained that **Rh-cat** could affect, in a reproducible manner, the size distribution of the nanospheres of the obtained polyphenylacetylenes [44].



Scheme 18:

7 Catalytic activity of Ru-cat

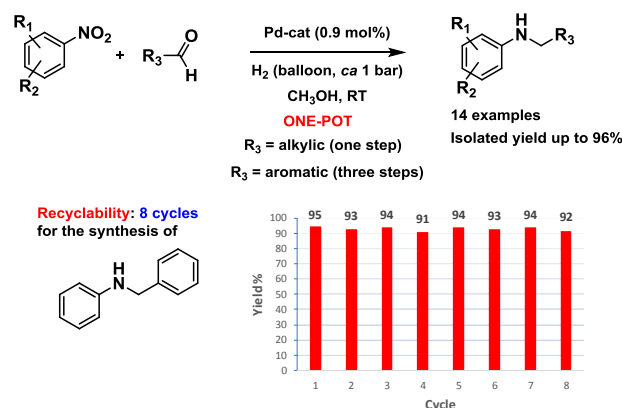
By copolymerizing the complex Ru(PPh₃)₂(AAEMA)₂ with DMAA as comonomer and MBAA in DMF and in presence of AIBN at 60°C, the insoluble resin **Ru-cat** was obtained (Scheme 3) [45]. The catalytic figure of merit of **Ru-cat** were indeed modest: employing **Ru-cat** in the hydrogenation of alkenes in methanol at 65°C under 20 bar of H₂, a low TOF (16 h⁻¹) was achieved.

8 Catalytic activity of Pd-cat

Pd-cat is by far the most versatile and widely used catalyst among the family catalysts based on metal-containing AAEMA because it was able to accelerate several kinds of chemical reaction such as reduction, oxidation and carbon-carbon bond forming reactions as well as esterification and transesterification reactions. Its synthesis requires the use of comonomer not containing nitrogen [37] and was achieved in very reproducible way by reacting Pd(AAEMA)₂, ethyl methacrylate (EMA) and ethylene glycol dimethacrylate (EGDMA), this latter added in portions, in THF under the light of a table lamp in the presence of AIBN [46].

The first catalytic application of **Pd-cat** in a reduction reaction was the hydrogenation of several unsaturated substrates such as olefins, alkynes, unsaturated aldehydes, citral, carvone, and nitro compounds under H₂ atmosphere at RT (Table 3) [47].

In most cases, the yields exceeded 90% within very short time reactions. Only benzaldehyde (entry 11 and 12) needed higher H₂ pressure to be first transformed into benzyl alcohol (*t* = 1 h) and then into toluene (4 h).



Scheme 19:

The refractoriness of benzaldehyde to be reduced prompted us to employ **Pd-cat** as a novel heterogenous catalyst in the one-pot direct amination reaction [48] using molecular hydrogen as reducing agent (Scheme 19) [49].

The catalytic system was found to be applicable, with slight differences, to both aliphatic and aromatic aldehydes and to a wide range of nitroarenes. Excellent yields of secondary amines were obtained under very mild conditions and the catalyst was recyclable at least 8 times without appreciable loss of activity and selectivity. TEM (transmission electron microscopy) analyses of **Pd-cat** demonstrated that the active species are insoluble palladium nanoparticles having a size distribution centred at 5 nm.

In looking for an eco-friendly and economic catalytic system for the reduction of nitroarenes to arylamines, we also found that **Pd-cat** could catalyse such reduction in

Table 3: Hydrogenation of unsaturated substrates catalyzed by **Pd-cat** (0.625% mol) at RT.

Entry	Substrate	solvent	P (bar)	Time (h)	Product	Yield (%)
1	1-heptene	CH ₃ OH	1	2	<i>n</i> -heptane	>99
2	cyclohexene	CH ₃ OH	1	2	cyclohexane	>99
3	1-octyne	CH ₃ OH	1	5	<i>n</i> -octane	77
4	phenylacetylene	CH ₃ OH	1	7	ethylbenzene	99
5	diphenylacetylene	CH ₂ Cl ₂	1	5.5	1,2-diphenylethane	>99
6	2-cyclohexen-1-one	CH ₃ OH	1	2	cyclohexanone	91
7	2-cyclopenten-1-one	CH ₃ OH	1	3	cyclopentanone	>99
8	cinnamaldehyde	CH ₂ Cl ₂	1	33	3-phenylpropanal	83
9	citral	CH ₃ OH	1	10.5	citronellal	70
10	(-)-carvone	CH ₃ OH	1	7	carvotanmenthone	70
11	benzaldehyde	CH ₃ OH	10	1	benzyl alcohol	95
12	benzaldehyde	CH ₂ Cl ₂	10	4	toluene	>99
13	nitrobenzene	CH ₃ OH	1	7	aniline	>99
14	2-nitrotoluene	CH ₃ OH	1	7	<i>o</i> -toluidine	>99
15	2,4-dinitrotoluene	CH ₃ OH	1	49	2,4-diaminotoluene	>99

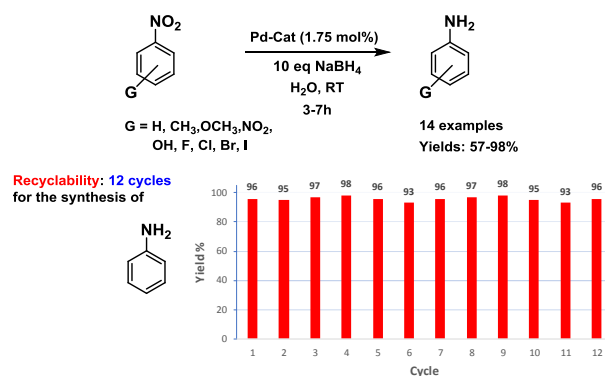
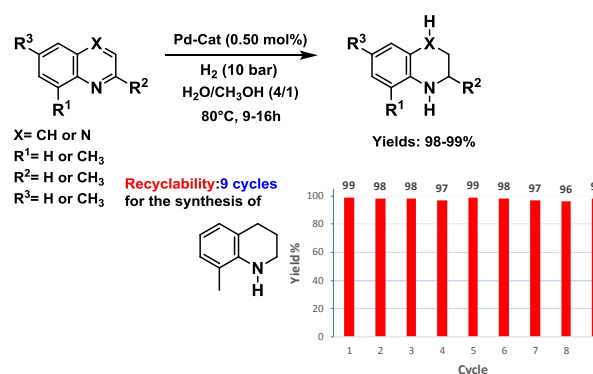
the presence of NaBH₄ and water as a mild reducing agent and a green solvent, respectively (**Scheme 20**) [50].

From moderate to excellent yields of aryl amines were obtained and the catalyst was recyclable at least 12 times without loss of activity and selectivity. In fact, TEM observations showed that the catalytic active species are very small Pd nanocrystallites (mean size diameter ca. 3 nm) formed in the presence of NaBH₄.

The activity of **Pd-cat** in reduction reactions was also tested in the reduction of quinolines to 1,2,3,4-tetrahydroquinolines, which are important intermediates for the synthesis of biological active molecules, drugs, agrochemicals, dyes, and alkaloids [51]. However, the selective catalytic hydrogenation of polynuclear heteroaromatic nitrogen compounds such as quinolines is a difficult task because quinolines usually poison the traditional noble metal-based hydrogenation catalysts. [52-54] In spite of these assumptions, **Pd-cat** was found an active and selective catalyst for reduction of quinolines and quinoxalines (**Scheme 21**) [55].

In aqueous medium, high yields and excellent selectivity were achieved under not severe conditions (80°C and 10 bar of H₂). The catalytic system maintained its activity and selectivity for nine cycles with negligible metal leaching. TEM analyses on catalyst pointed out that the active species were supported Pd nanoparticles, having a mean size of 4 nm, which did not aggregate with the recycles.

Searching for an eco-friendly and more economic catalytic system for the reduction of quinolines to

**Scheme 20:****Scheme 21:**

1,2,3,4-tetrahydroquinolines under milder conditions, we found that **Pd-cat** catalysed the reduction of quinolines in the presence of NaBH_4 as a mild reducing agent and neat water as green solvent (**Scheme 22**) [56].

Although a slightly higher **Pd-cat** loading (2.0 mol %) was necessary, the catalytic system exhibited excellent activity and selectivity, which were maintained for at least seven reaction runs without metal leaching. By means of TEM studies, it was ascertained that the active species were supported Pd nanoparticles, having a smaller mean size (3 nm) with respect to the protocol under H_2 pressure.

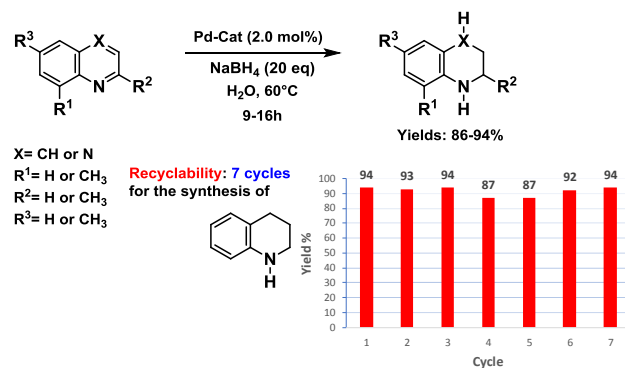
The first application of **Pd-cat** in accelerating a carbon-carbon bond forming reaction was the Heck cross-coupling reaction [57-59] between aryl iodides or bromides and different olefins, in the presence of potassium or sodium acetate as base (**Scheme 23**), in which **Pd-cat** also acted as phosphane free catalyst [60].

A very low **Pd-cat** loading was necessary to achieve *trans* disubstituted-olefins in moderate to excellent yields and the catalyst was recycled up to six times with slight loss of its activity. However, when the reaction mixture was hot filtered at 20% conversion of aryl halide, the activity of the mother liquor was almost comparable to that of fresh **Pd-cat**. On the other hand, if the filtration was carried out at 100% conversion of aryl halide, the activity of mother liquors was experimentally negligible. Thus, **Pd-cat** behaved as a reservoir of catalytically active palladium soluble species, which deactivated when the aryl halide was consumed [61].

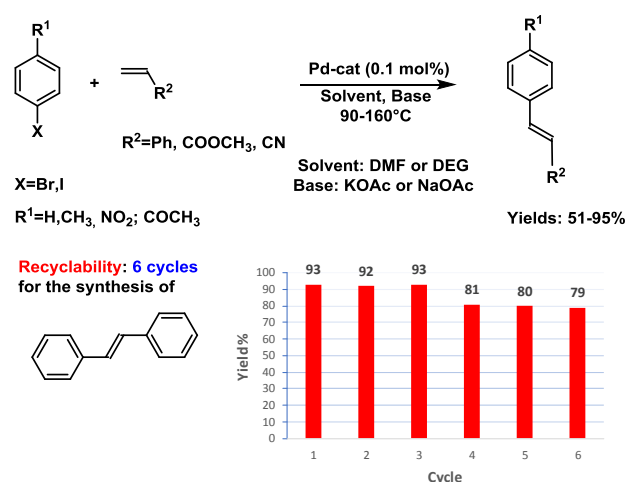
This behaviour was found to be not operating in the asymmetric allylic alkylation reaction [62-64] promoted by **Pd-cat** in the presence of catalytic amount of chiral ligands, such as (*R,S*)-PPFA, (*R,S*)-JOSIPHOS, and (*R,R*)-NORPHOS (**Scheme 24**) [65].

The reaction between *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate in the presence of *N,O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc provided good yields and good enantioselectivity (*er* up to 96.5:3.5 in the presence of (*R,S*)-JOSIPHOS). However, only when chiral ferrocenyl ligands (*R,S*)-PPFA and (*R,S*)-JOSIPHOS) were employed, **Pd-cat** could be used in two subsequent runs with a severe metal leaching (for (*R,S*)-JOSIPHOS: 71% yield and *er*= 92.5/7.5 in the recycle but metal leaching up to 39% of initial amount). Furthermore, in the case of (*R,R*)-NORPHOS the metal leaching after the first cycle is already almost quantitative.

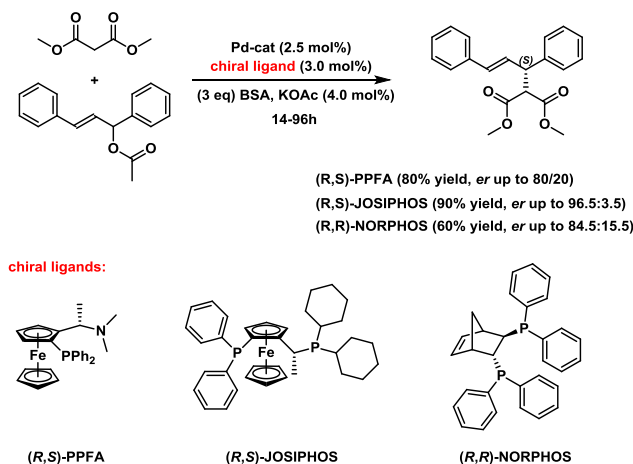
Pd-cat also displayed high efficiency in the Stille cross-coupling [66,67] of aryl iodides or bromides with various trimethyltin or tributyltin derivatives (**Scheme 25**) [68].



Scheme 22:



Scheme 23:



Scheme 24:

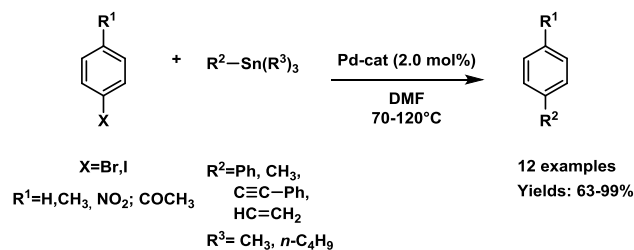
Yields from 63 to 99% were achieved in first cycle. In the case of aryl iodides, the catalyst was recycled up to six runs with appreciable lowering of catalytic activity due to the accumulation of tin derivatives onto the support, which hampered the migration of the substrates to the catalytically active sites.

Pd-cat was also successfully used as catalyst in the Suzuki-Miyaura cross-coupling reaction [69-72] of aryl bromides (or activated aryl chlorides) under air in neat water at 100°C, in the presence of K_2CO_3 as base (**Scheme 26**) [73].

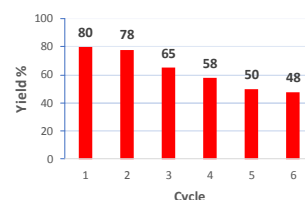
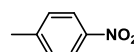
From good to excellent yields in biaryls were achieved and the catalyst was recycled at least five times without suffering from a significant palladium leaching. By means of hot filtration tests of the mother liquors, we established that **Pd-cat** acted as a reservoir of catalytically active species (palladium nanoparticles) that leached out in a very little amount for each cycle in solution. The use of a transfer phase agent, such as tetrabutylammonium bromide (TBAB) accelerated the cross-coupling reaction because it facilitated the formation of smaller size (more active) palladium nanoparticles.

The good activity and reusability of **Pd-Cat** in water media for the reduction of nitroarenes or quinolines with H_2 or $NaBH_4$ as reducing agent, and for the Suzuki-Miyaura cross-coupling reaction pushed us to perform a detailed and accurate studies on palladium nanoparticles formed during their catalytic runs. By combining information obtained through high-resolution TEM, X-ray energy dispersive spectroscopy, and micro-IR spectroscopy we were able to study the morphological features of the Pd nanoparticles formed in **Pd-cat**, before and after its use in catalysis, and also the effect on their evolution in function of several parameters, such as different reducing agents (aryl boronic acid, dihydrogen, $NaBH_4$), the presence of a phase transfer (TBAB) and the temperature [74]. Micro-IR spectroscopy showed that the support was chemically stable over the catalyst recycles in all the reactions tested, while TEM analyses pointed out that the macroporosity of the resin remained constant after each run and in all cases the pristine Pd(II) polymer supported complex was reduced *in situ* to Pd(0) forming nanoparticles (the active species) under reaction conditions. The organic support was always able to stabilize Pd nanoparticles during recycling without negligible agglomeration. High temperatures (80–100°C) favoured the formation of Pd nanoparticles of 9 nm average size, while at room temperature the Pd nanoparticles average size was smaller (2–6 nm).

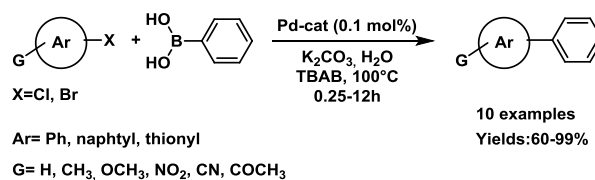
The presence of a phase transfer agent (TBAB) led to formation of Pd nanoparticles with 4 nm average size,



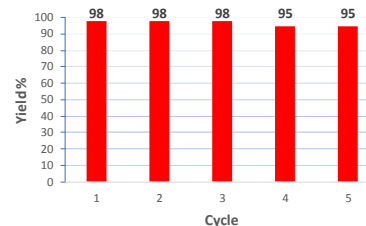
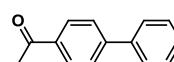
Recyclability: 6 cycles
for the synthesis of



Scheme 25:



Recyclability: 5 cycles
for the synthesis of



Scheme 26:

which leached into solution because of the well-known capacity of TBAB to stabilize the nanoparticles favouring their solubilization [75-77].

Concerning the use of different reducing agents on Pd nanoparticles, in the Suzuki-Miyaura coupling, the effect of the reductant such as aryl boronic acid was masked by the temperature reaction (100°C) and/or by the presence of TBAB (when used). On the contrary, for the reduction of nitroarenes or quinolines in water, the choice of the reductant (H_2 or $NaBH_4$) was fundamental to determinate the diameter size of Pd nanoparticles. Under H_2 atmosphere, Pd nanoparticles with average diameter size from 6 to 10 nm were obtained, while in the presence of $NaBH_4$ they ranged from 2 to 4 nm.

By summarizing the investigation results, in Suzuki-Miyaura reaction **Pd-cat** operated as a reservoir of

soluble Pd nanoparticles, which were released into the aqueous environment and they were effectively recaptured by the polymer matrix after substrate consumption. In fact, TEM images of **Pd-cat** recovered after any recycles showed the majority of Pd nanoparticles onto the surface of the polymer. This “release and catch” mechanism of active species, is commonly accepted by the scientific community for some heterogeneously catalysed C–C bond forming reaction [78-80]. On the other hand, in the hydrogenation reactions under H₂ atmosphere or in the presence of NaBH₄, **Pd-cat** operated by means of a truly heterogeneous catalytic mechanism because TEM images of **Pd-cat** recovered after any recycles showed a uniform distribution of Pd nanoparticles in the polymer matrix.

Pd-cat acted as heterogeneous catalyst for the oxidation of alcohols in water by air. Primary and secondary aromatic alcohols were oxidized to their corresponding carbonyl compounds in excellent yields with a very low Pd loading (0.5 mol%) in relatively short reaction times (**Scheme 27**) [81].

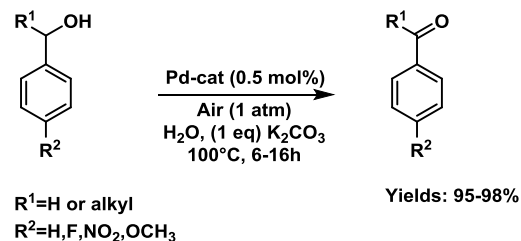
The catalyst was easily recovered and reused up to six cycles. Hot filtration tests indicated that **Pd-cat** really operated through a heterogeneous pathway.

Finally, **Pd-cat** was found to catalyse, under pressure of 2 bar of H₂ and in the presence of catalytic amount of bromobenzene in excess of alcohols, the esterification (or transesterification) of aliphatic and aromatic carboxylic acids into their corresponding esters in good to excellent yields (**Scheme 28**) [82].

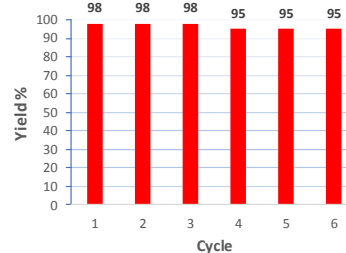
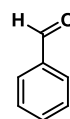
Bromobenzene was necessary to generate in-situ a little amount of HBr, which provided a mild acidic reaction environment. Under these reaction conditions the true active species were, again, stabilized Pd nanoparticles and **Pd-cat** was reusable for eight consecutive cycles with a negligible Pd leaching into solution. The catalytic system was also explored in preliminary studies for the preparation of partially hydrogenated fatty acid methyl esters, starting from a mixture composed by highly polyunsaturated esters and free carboxylic acids, taken as a model acidic feedstock for mimic a biodiesel upgrading [83,84].

9 Conclusions

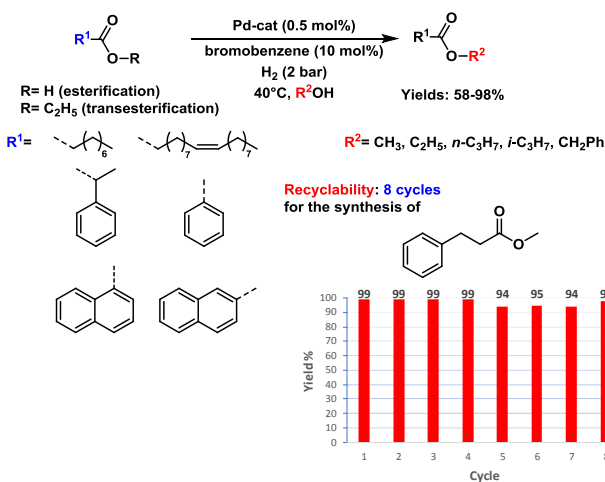
Polymerization of transition metal-containing the polymerizable ligand AAEMA turned out to be a convenient alternative tool for the preparation of supported transition metal catalysts as MCPs. These MCPs employed as catalysts in several kinds of chemical reactions showed



Recyclability: 6 cycles
for the synthesis of



Scheme 27:



Scheme 28:

high efficiency and/or excellent selectivity and very often they could be recovered and reused in multiple cycles without significant loss of their activity and selectivity. Soon, other catalytic applications will be explored for these catalysts and new noble or non-noble transition metal-containing AAEMA will be synthesized and then polymerized with suitable comonomers and crosslinkers to obtain novel catalysts. Much efforts will be made to systematically ascertain when the solid matrix not only possess the role of heterogenizing the catalyst but also when it affects the chemical efficiency and the selectivity of a chemical process.

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Conflict of interest: Authors state no conflict of interest.

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