POLYMER-SUPPORTED POLYMERIZATION CATALYSTS *VIA* ROMP

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SUMMARY: Recent developments in the synthesis of heterogeneous catalytic supports are reported. In combination with grafting and precipitation polymerization techniques, ring opening metathesis polymerization (ROMP) has been applied to the synthesis of surface-functionalized inorganic and organic supports. Applications of these well-defined heterogeneous catalytic supports in C-C coupling reactions (Heck couplings) as well as in atom-transfer radical polymerization (ATRP) are reported.

Introduction

The synthesis of well-defined catalytic supports with an exactly defined and stable surface chemistry is still an intensively investigated area. In order to avoid catalyst poisoning and unwanted side reactions, such high definitions are a basic requirement in heterogeneous catalysis. Standard functionalization procedures of *organic* supports often use *divergent* synthetic approaches that entail a step by step transformation of surface-bound functional groups. Ill-defined systems result from the fact that these transformations usually do not proceed in a quantitative way. In order to avoid this, we elaborated a conceptually new approach based on metathesis precipitation polymerization[1] that allows the synthesis of such supports by a *convergent* synthetic route, starting from functional monomers. In addition, ring-opening metathesis *grafting* polymerization was applied to the synthesis of heterogeneous catalytic supports. In the following, a few recent examples in ATRP and C-C coupling chemistry will be presented that illustrate the general usefulness of the ROMP-based concepts.

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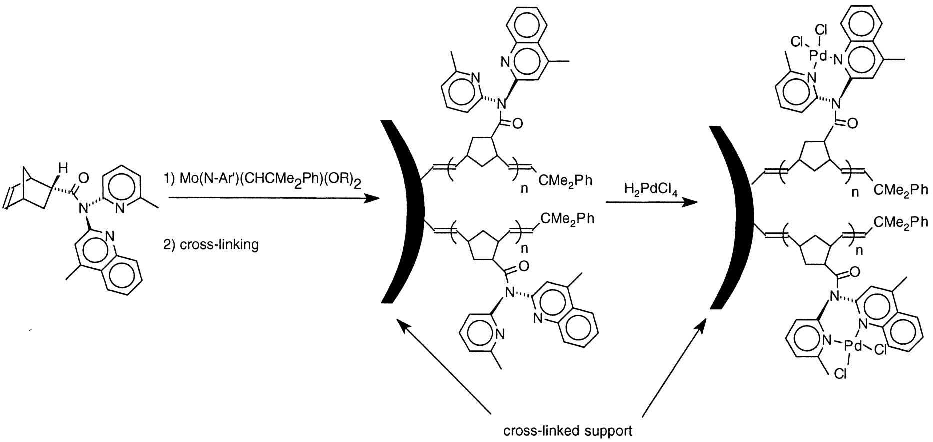
Heterogeneous Heck systems *via* ring-opening metathesis precipitation polymerization

There exist a vast variety of different Pd-based systems for the vinylation of aryl halides, commonly called Heck systems[2]. Despite the significant progress in homogeneous catalysis[3, 4], the demand for highly active and stable heterogeneous systems is still high. Highly active systems may be generated from phosphine- or aminophosphine-based ligands[5], yet these are easily transformed into the corresponding phosphine oxides, which somehow limits their general applicability. Consequently, phosphane-free ligands are of particular interest[6-8]. Ligands solely based on nitrogen[9], e. g. dipyridyl amide-based systems, are relatively rare, yet turned out to be suitable for the synthesis of highly temperature stable and active Heck catalysts[10]. If incorporated into suitable monomers, ring-opening metathesis precipitation polymerization using Schrock initiators may be used for the preparation of well-defined heterogeneous Heck systems based on such ligands[10]. The adherent polymerization system must fulfill a class VI living system[11]. Subsequent cross-linking of the "living" linear polymer chains by a suitable norbornene-based cross-linker in course of the precipitation polymerization leads to the formation of irregularly shaped polymer beads (Scheme 1)[12]. Even complex functionalities may be introduced with high reproducibility and without any change in the chemical nature, geometry and even absolute configuration of the corresponding functional group. Generally speaking, heterogeneous polymer supports prepared by this approach are characterized by an exact knowledge about the chemical structure of the actual catalytic sites and a high density of functional groups at the surface. The amount of functional monomer immobilized by this approach may be varied within a range of 0 – 1 mmol/g. Table 1 gives an overview over the beaded materials. The particles have a mean diameter of 20 - 40 µm, and are generally characterized by a low specific surface area ($4 < \sigma < 30$ m^2/g). As a consequence of the polymerization order, the linear polymer chains bearing the functional groups form tentacles that are attached to the surface of the cross-linked carrier (Scheme 1). This ensures a fast mass transfer with any kind of mobile phase or liquid and lets these materials appear as highly attractive for extraction and immobilization purposes.

Table 1. Summary of poly(norbornene-5-dipyridyl carbamide) ($C(O)Npy_2$)-functionalized resins[12, 13].

Cat.	**functional group**	**capacity [mmol/g]**
1	N,N-dipyrid-2-ylcarbamide	1.0
2	N,N-dipyrid-2-ylcarbamide	0.6
3	N-pyrid-2-yl-N-(3-methylpyrid-2-yl)carbamide	0.03
4	N-pyrid-2-yl-N-(6-methylpyrid-2-yl)carbamide	0.05
5	N-(6-methylpyrid-2-yl)-N-(4-methylquinolin-2-yl)carbamide	0.05

Cross-linker = 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (DMNH6).



Scheme 1. Synthesis of derivatized polymer beads based on substituted dipyridyl amides *via* ROMP [12]. Cross-linker = DMNH6.

These dipyridyl carbamide-based materials may be used as supports for heterogeneous catalysis as they represent typical small-particle catalysts[14]. Thus, the palladium-loaded chelating groups are located exclusively at the surface of the particle, they are easily accessible, diffusion plays a minor role and coupling reactions proceed within the interphase[15].

Table 2. Summary of Heck-couplings and polymerizations[10]. TBAB = tetrabutylammonium bromide. T = 140 °C, t = 90 h. For further experimental conditions refer to [10, 16].

Ar-X	**$H_2C{=}CHR$**	**product**	**cat.**	**yield [%]**	**TON x 10^3**
iodobenzene	styrene	*trans*-stilbene	**1**	99	111.0
iodobenzene	styrene	*trans*-stilbene	**3**	91	31.9
iodobenzene	styrene	*trans*-stilbene	**4**	96	33.6
iodobenzene	styrene	*trans*-stilbene	**5**	92	32.2
iodobenzene	ethyl acrylate	ethyl cinnamate	**1**	75	175.1
iodobenzene	ethyl acrylate	ethyl cinnamate	**3**	87	213.2
iodobenzene	ethyl acrylate	ethyl cinnamate	**4**	91	223.0
iodobenzene	ethyl acrylate	ethyl cinnamate	**5**	89	218.1
bromobenzene	styrene	*trans*-stilbene	**1**	90	40.0
bromobenzene	styrene	*trans*-stilbene	**3**	6	2.5
bromobenzene	styrene	*trans*-stilbene	**4**	35	14.4
bromobenzene	styrene	*trans*-stilbene	**5**	31	12.8
4-bromobenzonitrile	styrene	4-cyano-*trans*-stilbene	**1**	83	157.7
4-bromobenzonitrile	styrene	4-cyano-*trans*-stilbene	**3**	36	67.6
4-bromobenzonitrile	styrene	4-cyano-*trans*-stilbene	**4**	34	63.8
4-bromobenzonitrile	styrene	4-cyano-*trans*-stilbene	**5**	33	62.0
4-bromo-1-fluorobenzene	styrene	4-fluoro-*trans*-stilbene	**1**	58	34.4
4-bromo-1-fluorobenzene	styrene	4-fluoro-*trans*-stilbene	**3**	38	22.2
4-bromo-1-fluorobenzene	styrene	4-fluoro-*trans*-stilbene	**4**	41	23.9
4-bromo-1-fluorobenzene	styrene	4-fluoro-*trans*-stilbene	**5**	21	12.3
4-Cl-acetophenone/TBAB	styrene	4-acetyl-*trans*-stilbene	**1**	95	6.1
4-Cl-acetophenone/TBAB	styrene	4-acetyl-*trans*-stilbene	**3**	18	1.1
4-Cl-acetophenone/TBAB	styrene	4-acetyl-*trans*-stilbene	**4**	34	2.1
4-Cl-acetophenone/TBAB	styrene	4-acetyl-*trans*-stilbene	**5**	20	1.2

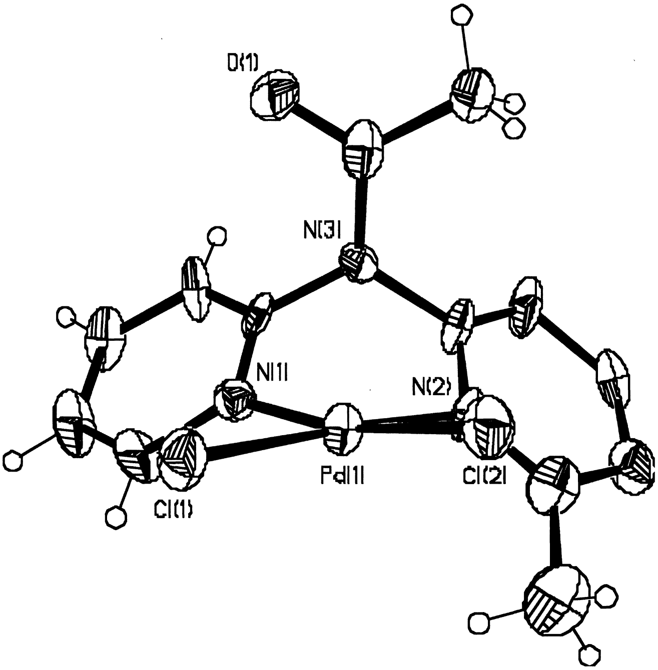


Figure 1. X-ray structure of dichloropalladium-N-acetyl-N-pyrid-2-yl-N-6-methylpyrid-2-ylamine.

Active species

As can be deduced from Table 2, variation of the ligand structure leads to drastic changes in the reactivity. Thus, the unsubstituted, parent dipyrid-2-yl amide based initiator was highly active (94 - 99 % yields) in the vinylation of aryl iodides and aryl bromides (Heck couplings) with turn-over numbers (TONs) of up to 210 000[10]. High yields (≤ 95 %) and TONs (≤ 24 000) may additionally be achieved in the tetrabutylammonium bromide (TBAB) assisted vinylation of aryl chlorides (Table 2). While coupling yields and TONs achieved with the substituted ligands in the Heck coupling of aryl iodides were still comparable, different results are obtained in the C-C coupling of aryl bromides and chlorides. Thus, changing from aryliodides to the less reactive aryl bromides leads to lower coupling yields and TONs. Coupling yields for bromobenzene and the more active 4-fluoro- and 4-cyano-substituted analogues were in the range of 33 – 41%, TONs of 21000 – 68000 were achieved. In order to elucidate this situation, the stability constants of compounds **3** – **5** as well as x-ray investigations were conducted. Values for K_D in the corresponding N-acetyl derivatives were found to be in the range $9 \cdot 10^{-5}$ – $5 \cdot 10^{-2}$ mol/l. This reduced stability (K_D of the parent, unsubstituted system is $< 10^{-6}$) is explained by the distorted geometry that e. g. results from interactions of the methyl group with one of the chlorine atoms (Figure 1). The reactivity of supports **3** – **5**, respectively (Table 2) is directly related to these geometric and thermodynamic features. While the methyl group in 3-position (support **3**) basically has no influence on the reactivity, the methyl group in position 6 (supports **4** – **5**) drastically reduces the stability of these catalytic systems. Consequently, coupling results obtained with these compounds are similar to those of $Pd(OAc)_2$.

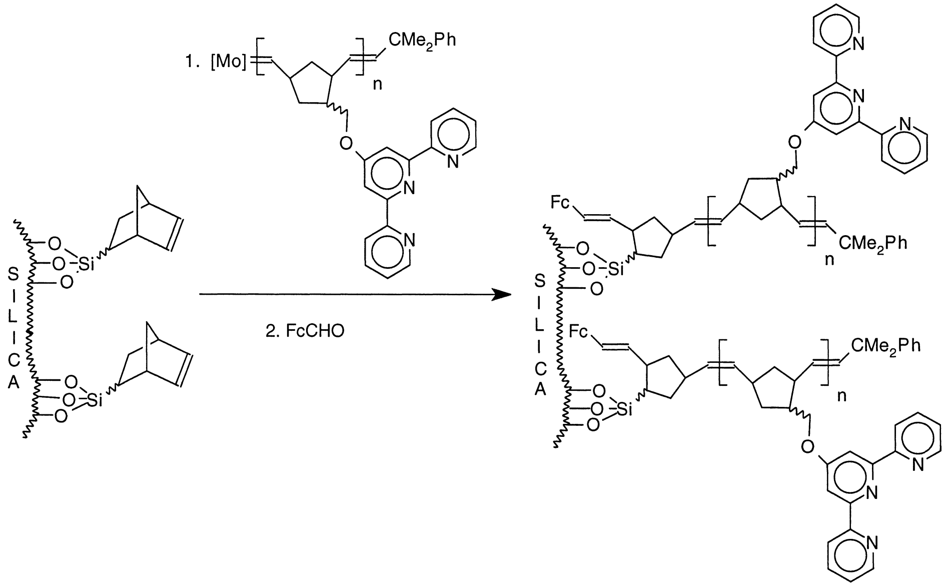
Neutral or anionic palladium (0) species are widely accepted to represent the active species in Heck type couplings. They are generated by a redox-reaction[17] e. g. *via* oxidation of a phosphine to the corresponding phosphine oxide[18, 19]. Recently, Arai et al. proposed that Pd (0) that leached into a suitable solvent from a support essentially catalyzes the reaction[20, 21]. Both the base and the solvent influence the kinetics of the reaction, yet do not affect the overall rate of the reaction much. Based on the reduced stability of the Pd-complexes and on the observed coupling activities we believe that such dissolved Pd species play an important role in the present system.

Heterogeneous ATRP supports *via* ring-opening metathesis graft-copolymerization

Living radical polymerizations[22-24] and in particular atom transfer radical polymerization (ATRP) [25] have gained significant interest during the last years. Such polymerizations may be carried out in a "quasi-living"[11, 22, 26-28] manner and allow the presence of certain functionalities[29-31]. Despite the simplicity of this approach, the resulting polymers suffer from high metal contents due to the homogeneous approaches that are used in most cases. Due to the encouraging results obtained with heterogenized Heck-coupling systems[10, 32], a new

ROMP-based access to well-defined, highly active heterogeneous polymer supports for ATRP[33, 34] was elaborated.

For these purposes, norborn-2-ene-derivatized silica-based supports were prepared by silanization employing norborn-2-ene-5-yltrichlorosilane. Surface grafting of the norbornene-modified supports with a series of dipyridylamide and terpyridine-containing chelating monomers was accomplished using ROMP (Scheme 2). A multi-point attachment grafting method as described earlier[35] was applied.



Scheme 2. Ring-opening metathesis graft copolymerization[35]. Initiator = Mo(N-2,6-*i*-Pr_2-C_6H_3)($CHCMe_2Ph$($OCMe(CF_3)_2$)$_2$. Fc = ferrocenyl.

ATRP systems based on dipyridylamides and terpyridines represent mono-ligated metal centers. Since the equilibrium M^{n+} <-> M^{n+1} that is involved in this type of reactions does not require any conformational changes or dissociation of a ligand, polymerization proceeds comparably fast. Thus, maximum monomer conversion is already achieved within 2 hours. The general results obtained with ROMP-based heterogeneous polymerization systems may be summarized as follows. (i) Both dipyridylamide and terpyridyl-based monoligated systems may be used in ATRP. (ii) Complexes that contain the reduced species of the corresponding metal (preferably Cu) were found to work best and additionally avoid the use of a reducing agent (e. g. MAO, Al(*i*-OPr)$_3$). (iii) poly(styrene) may be prepared up to a M_w of 80,000 in 20 – 30 % yield. Polydispersities vary from 1.5 – 1.9. These polymers are virtually metal free as determined by atom absorption spectroscopy (metal content < 100 ng/g). (iv) Polymerizations proceed fast, yet level off after approximately 2 hours at monomer consumption < 35 %. In principle, polymerization may cease due to deactivation or recombination of the radicals. Based on the fact that polymerization yields are neither influenced by the addition of further initiator and/or Al(*i*-OPr)$_3$ nor by any change of the nature of the support, we tentatively ascribe the low polymerization yields to unfavorable rate constants of deactivation (k_d). This leads to a situation, where a high concentration of radicals is produced *via* rapid initiation without the opportunity of forming the dormant species. Since the time for an average termination step is the reciprocal of the product of the termination rate coefficient (k_t) and the concentration of the radicals ($t_a = 1/k_t[P^*]$)[36], termination is fast in such systems. This is in accordance with the finding that tertiary initiators such as ethyl-2-bromo-*i*-butyrate react fast compared to their secondary or primary analogues, thus providing high radical concentration[37].

Conclusions

It has been demonstrated that ROMP represents a highly versatile tool in the preparation and modification of functional polymer supports. The use of well-defined initiators allows the highly reproducible preparation of tailor-made materials in particular in terms of functionalization. Various polymerization techniques such as precipitation- and graft-polymerization may be applied.

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