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Immobilization of ruthenium(II) salen complexes on poly(4-vinylpyridine) and their application in catalytic aldehyde olefination

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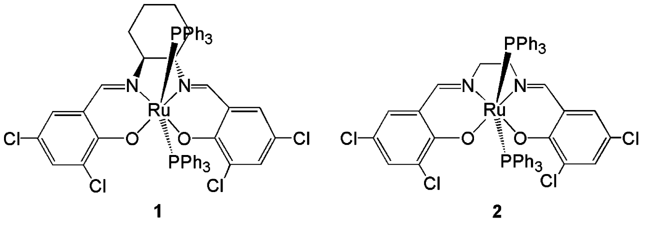
Abstract—Two Ru(II)(salen)$(PPh_3)_2$ complexes grafted on poly(4-vinylpyridine) have been synthesized and characterized. An elemental analysis shows that both grafted samples contain ca. 0.6 wt % Ru. FTIR spectra confirm the formation of metal–salen complexes attached to the carrier polymer by an interaction between the ruthenium(II) compounds with the pyridine nitrogen atoms of the poly(4-vinylpyridine). Immobilization of both Ru(II) salen complexes on the polymer increases their thermal stability as demonstrated by TG–MS analysis. The grafted materials were applied as catalysts for the olefination of various aldehydes at 60 °C under an inert gas atmosphere, showing comparable yields as their homogeneous congeners and high trans-selectivities. The ruthenium(II) compound with a larger salen ligand shows a better recyclability and selectivity than the derivative with the smaller ligand.

1. Introduction

Many of the so called salen ligands can be easily substituted, ligated to a broad variety of transition metals and applied in several catalytic reactions.[1–4] It has been reported, for example, that different types of ruthenium(II) salen complexes (Scheme 1) are successfully applicable as catalysts for the olefination of a broad variety of aldehydes in homogeneous phase, displaying very good results and selectivities.[5] Their high catalytic activity is probably due to the flexibility of the ethylenediamine backbone of the salen ligands as described for a number of transition metal complexes with bidentate oxygen ligands.[6] However, a drawback of using metal salens in homogeneous solutions is the formation of μ-oxo dimers and other polymeric species leading to irreversible catalyst deactivation. In principle, this problem can be treated by isolating the metal–salen complexes from each other by encapsulating them in the cavities of molecular sieves. By applying this method, the isolated catalytic active centres will not undergo so rapid degradation as their homogeneous counterparts do.[7–9] However, the leaching of active catalyst is nevertheless occurring to a certain degree and responsible for a decrease in activity during recycling experiments.[10] In order to overcome problems of that kind, the utilization of polymer-supports has attracted a significant attention, due to the stability and uniformity of the obtained materials, and the possibility of easier product/catalyst separation, combining the advantages of homogeneous and heterogeneous catalysis. Such systems containing immobilized organometallic (catalyst) compounds have several advantages, such as the simple recycling of the catalysts by filtration, preventing the loss of both ligands and (heavy) metal, thus considerably decreasing the environmental problems of waste materials, in comparison to homogeneous catalysis.[11,12]



Scheme 1. Synthesized ruthenium(II) salen complexes.

Keywords: Catalysis; Heterogenization; Olefination; Polymer; Ruthenium.

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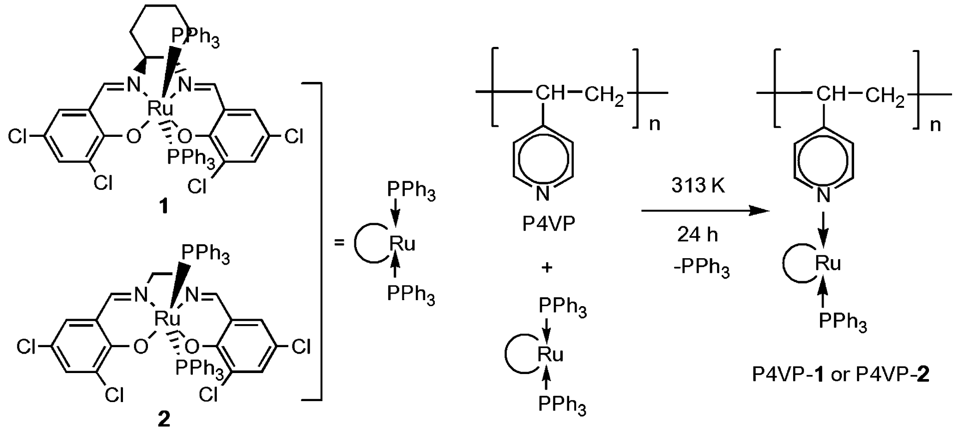


Scheme 2. Grafting of complex 1 and 2 on P4VP.

In the present work, both ruthenium(II) salen compounds of formula **1** and **2** were immobilized on poly(4-vinylpyridine) (P4VP) under an inert gas atmosphere at 60 °C (Scheme 2). The grafted polymer materials are designated as P4VP-**1** and P4VP-**2**. The obtained new materials have been applied as catalysts for aldehyde olefination using diazoethylacetate (EDA) and different aldehydes/ketones. The activities in catalysis of the systems are compared.

The ruthenium-loading of the two complexes grafted on P4VP determined by elemental analyses (EA) is ca. 0.6 wt % in both cases.

The intense stretching vibrations of the pyridine rings appear at ca. 1598 cm^{-1} (dotted line) for pure P4VP. However, due to the presence of the coordinated ruthenium(II) ions in the polymer as illustrated in Scheme 2, the pyridine stretching vibrations intensities clearly decrease.[15–17] The most important finding in this respect is that for both grafted materials the imine stretching vibration of the metal salen moiety is found at ca. 1615 cm^{-1}. A weak absorption of the salen ligand at 1500 cm^{-1} and several new peaks can be observed in the grafted materials, evidencing the presence of the complexes on the polymer material[18] (see Fig. 1). Only insignificant shift changes of the bands associated with the ligand stretching modes are observed. These slight deviations (<10 cm^{-1}) are more likely caused by the ligand distortion due to immobilization in the polymer backbone.[19]

In the TG–MS spectra, complex **1** displays its first decomposition onset at 205 °C followed by a second decomposition onset observable at 250 °C. The associated mass losses amount to ca. 44%. These mass losses correspond to the loss of two triphenylphosphine ligands (48% of the total mass of compound **1**). This interpretation is further supported by mass spectroscopy (MS) of the fragments observed during the decomposition process (TG–MS) showing the fragmentation patterns of triphenylphosphine ligands. The third decomposition step starts at 468 °C and corresponds to a mass loss of ca. 28% of the original mass. This decomposition step accounts very likely for the fragmentation of the salen ligand. This assumption is again supported by mass spectroscopy. The remaining residue consists mainly of ruthenium chloride (24% of the original mass). Complex **2** shows a higher thermal stability than compound **1** (decomposition onset at 258 °C) and decomposes also in three steps. For both grafted complexes, the main degradation step starts at ca. 350 °C and finishes at ca. 450 °C. The total weight losses of P4VP-**1** and P4VP-**2** amount to 82 and 81 wt %, respectively, within the examined temperature interval (323–1273 K). According to the obtained mass spectra and the elementary analysis of the residue, the decomposition of compound P4VP-**2** starts with the loss of the phosphine ligands and finally leaves only ruthenium chloride. Clear separations between the different degradation steps cannot be observed in the case of P4VP-**2**. It can be concluded that the grafted complexes are more thermally stable than their homogeneous counterparts.

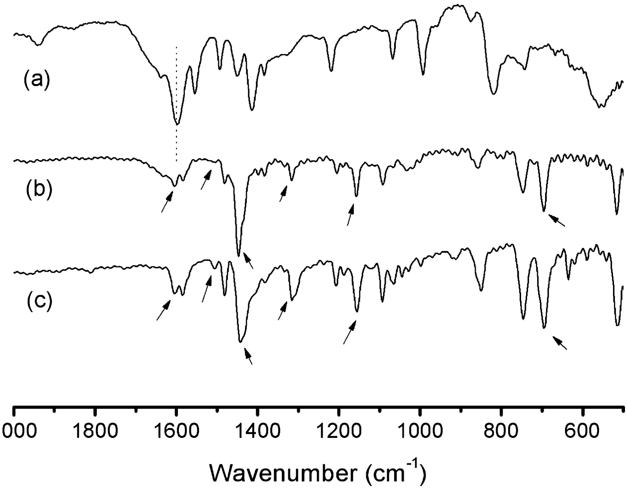
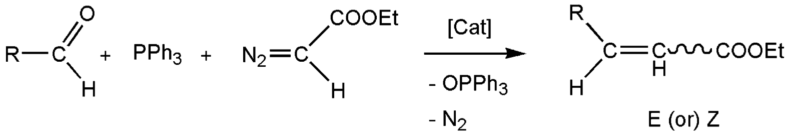


Figure 1. FT-IR spectra of pure P4VP (a), P4VP-**1** (b) and P4VP-**2** (c).

DSC analyses of the P4VP, P4VP-**1** and P4VP-**2** reveal the T_g-value of P4VP being 144 °C. The mobility of the polymer chains is restricted by physical cross-linking and, thus, leads to higher glass transition temperatures relative to that of the parent polymer (without cross-linking). Generally, the value of T_g increases upon the

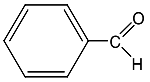
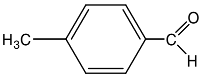
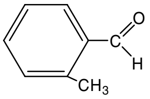
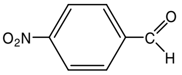
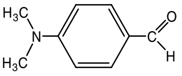
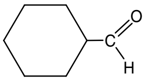


Scheme 3. General equation for the (catalyzed) aldehyde olefination reaction.

addition of the complex because of the increase of metal–polymer interactions.[20] It is clearly seen that the heterogenization of complex **1** and complex **2** on the polymer has increased the T_g value in comparison to P4VP to 184 and 168 °C, respectively.

P4VP-**1** and P4VP-**2** were found to be active as catalysts for the olefination of various aldehydes with EDA at room temperature (Scheme 3) as summarized in Table 1. All applied aldehydes either are not activated (Table 1, entries 1–3) or electron deficient (Table 1, entry 4) with the exception of the electron rich dimethylamino benzaldehyde, where product yields of >50% can be reached within 24 h at 60 °C. The sterics of *o*-methylbenzaldehyde seem to play a significant role to increase the yield under the applied conditions (Table 1, entry 3). This observation may be related to the three-dimensional and the long chain structure of P4VP providing a molecule trap, which is beneficial to maintaining the interaction between the bulkier substrates and the active site of the catalysts (ruthenium metal centre).[21]

Table 1. Olefination of various aldehydes using EDA with heterogeneous complexes P4VP-**1** and P4VP-**2**[a]

Olefin	Yield[b] (%) and selectivity (cis:trans)[c]	
	P4VP-**1**	P4VP-**2**
	63 (5:95)	84 (6:94)
	51 (1:99)	90 (2:98)
	70 (5:95)	56 (6:94)
	96 (1:99)	78 (1:99)
	12 (0:100)	12 (0:100)
	55 (2:98)	69 (3:97)

[a] Reactions were carried out in 5 ml of THF with 1 mol % of catalyst (based on the Ru-loading) of P4VP-**1** or P4VP-**2**, 0.25 mmol of aldehyde, 0.3 mmol of EDA and 0.3 mmol of PPh_3 at 333 K under argon. Reaction time = 24 h.

[b] Isolated yield.

[c] GC–MS measurement.

The presence of electron rich carbonyl groups in dimethylaminobenzaldehyde might lead to the remaining of intact substrate molecules on the active ruthenium(II) sites of the catalyst thus blocking these sites (Table 1, entry 5). Such a behaviour might contribute to the observed low yields since the reaction does not go to completion in these cases. Non-aromatic aldehydes, for example, a cyclic aldehyde (Table 1, entry 6), can also be catalyzed by both P4VP-**1** and P4VP-**2**.

P4VP-**1** and P4VP-**2** were recycled for several runs of benzaldehyde olefination as shown in Table 2. P4VP-**1** is much more stable and slightly more selective than P4VP-**2**. The higher stability of P4VP-**1** can be evidenced by leaching experiments where the filtered solution of P4VP-**1** and P4VP-**2** show product yields of 6% and 10%, respectively, after the separation from the catalyst materials at reaction temperature. The steric bulk of the salen ligand of complex **1** is larger than that of complex **2**. Immobilized on P4VP this may affect the stability and the selectivity of the grafted materials. The leaching of active catalyst of both P4VP-**1** and P4VP-**2** occurs to a certain degree and responsible for the decrease in activity during the recycling experiments due to the comparatively weak N → Ru interaction.

However, the degree of leaching is less pronounced in both cases than the leaching of ruthenium(II) salen complexes grafted on MCM-41 and SBA-15 as reported previously.[10] The adsorption of reactant/product molecules on the polymer surface together with the steric hindrance as a consequence of the presence of large size grafted complexes on the polymer certainly plays a role in

Table 2. Olefination of benzaldehyde using EDA with homogeneous complex **1** and complex **2** and heterogeneous P4VP-**1** and P4VP-**2**[a]

Catalysts	Run	Reaction time (h)	Yield[b] (%)
1		1.5	92
P4VP-**1**	First run	24	63
	Second run	24	58
	Third run	24	45
2		1.5	93
P4VP-**2**	First run	24	84
	Second run	24	51
	Third run	24	17

[a] Reactions were carried out in 5 ml of THF with 1 mol % of the catalyst (based on the Ru-loading) of homogeneous complex **1** or complex **2** and heterogeneous P4VP-**1** or P4VP-**2**, 0.25 mmol of aldehyde, 0.3 mmol of EDA and 0.3 mmol of PPh_3 at 333 K under argon.

[b] Isolated yield.

decreasing the catalytic activity during repeated runs. A noteworthy finding of this work is that the somewhat larger size (steric bulk) of a salen ligand seems to lead to a slightly better recyclability, beside its somewhat higher selectivity.[22–24] The lower degree of leaching compared to mesoporous carrier materials is an important advantage of the polymeric carrier materials applied in this work.

Two types of Ru(II) salen complexes are successfully grafted on the poly(4-vinylpyridine). The obtained heterogeneous catalysts are found to be of lower activity for the olefination of various aldehydes than the homogeneous compounds. The better recyclability of the polymer supported material, when compared to catalyst immobilized on mesoporous material is a noteworthy advantage, however. The ruthenium(II) compound ligated by a larger salen ligand shows a better recyclability and selectivity than that with the smaller ligand. An aim for future work will be the generation of a covalent surface-metal bond, possibly with an organometallic linker, which might further reduce leaching.

2. Experimental

2.1. Synthetic procedure

P4VP is used as provided by Aldrich without purification for the synthesis of the grafted materials. All the grafting procedures are carried out under an oxygen- and water free argon atmosphere using standard Schlenk techniques if not indicated otherwise. Dichloromethane (DCM) is dried over calcium hydride and kept over 4 Å molecular sieves. Tetrahydrofuran (THF) is dried over sodium and also kept over 4 Å molecular sieves.

Complex **1** and complex **2** were synthesized as described earlier.[13,14] Grafting experiments (Scheme 3) were carried out using standard Schlenk techniques under an argon atmosphere with the following procedure: 1 g of polymer [P4VP, 2% cross-linker] is dried under vacuum at room temperature and then 0.0814 g (0.075 mmol) of complex **1** or 0.0775 g (0.075 mmol) of complex **2** are introduced in the presence of 30 ml acetonitrile as solvent. The obtained mixture is stirred at 323 K for 24 h the resulting materials are washed several times with CH_2Cl_2 and dried at room temperature under vacuum. The grafted polymer materials are designated as P4VP-**1** and P4VP-**2**.

2.2. Characterization methods

IR spectra are measured with a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Microanalyses are performed at the Mikroanalytisches Labor of the Technische Universität München (U. Ammari and coworkers). Thermogravimetry, combined with mass spectroscopy (TG–MS) is conducted with a Netzsch TG209 system; typically about 10 mg of a sample were heated from 323 to 1273 K at a heating rate of 10 K min^{-1} under an argon atmosphere.

2.3. General procedure for aldehyde olefination in THF

In an oven dried Schlenk tube 1 mol % of the polymer grafted catalyst (based on the Ru-loading), aldehyde (0.25 mmol), PPh_3 (0.30 mmol) and 3.5 ml of THF were placed and heated to 60 °C in an oil bath. EDA (0.30 mmol), dissolved in 1.5 ml of THF, was added and then the mixture was kept for the times given in Table 1. The suspension was then cooled to room temperature and the solution was separated from the catalyst by filtration. Afterwards, the residue was concentrated and chromatographed over a silica gel column with *n*-hexane/ethyl acetate (20:1–8:1) affording the desired olefins.

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