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An Efficient Approach for Immobilizing the Oxo-Vanadium Schiff Base onto Polymer Supports using Staudinger Ligation

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Abstract: The present paper describes the use of Staudinger ligation as an efficient and high-yielding approach for the immobilization of oxo-vanadium Schiff base on polymeric supports *via* covalent attachment under mild conditions. The described strategy is simple in use, versatile, highly efficient with respect to better catalyst loading and proceeds under mild, metal-free conditions. The catalytic potential of the prepared polymer immobilized oxo-vanadium Schiff bases was tested for the oxidation of sulfides using aqueous *tert*-butyl hydroperoxide (TBHP) as oxidant. The polymer-supported catalysts could easily be recovered from the reaction mixture and reused for four runs without loss in activity and no metal leaching was observed during this course.

Keywords: oxidation; oxo-vanadium Schiff base; Staudinger ligation; sulfides; supported catalyst

Immobilization of metal complexes to polymeric support is an area of intensive research as these immobilized complexes offer a number of advantages over traditional solution-phase chemistry.[1] These supported complexes can easily be recovered from the reaction mixture, do not contaminate the product, can be recycled and enhance selectivity. The methods which are hitherto known for the immobilization of metal complexes onto the polymer support either involve the synthesis of polymer-bound ligands followed by complexation[2] or the direct reaction of the preformed metal complex with a functionalized polymer.[3] However, these methods suffer from certain drawbacks such as need for excess metal complex and reagents, slow reactions of metal complexes with polymer support, lower catalyst loading and harsh reaction conditions. To circumvent the limitations associated with the known methods, we focused our attention towards a new coupling strategy, calling only for the stoichiometric use of ligands or metal and providing high catalyst loading under mild reaction conditions.

Staudinger ligation,[4] a metal-free coupling strategy between an azide and appropriately substituted carboxylic acid mediated by trialkyl- or triarylphosphine in which a chemically stable amide bond is formed, proceeds under mild reaction conditions, almost quantitatively and without noticeable formation of side products. While Staudinger ligation has extensively been used for the immobilization of bioactive molecules,[5] to the best of our knowledge there is no literature report on its use for the preparation of polymer-bound metal catalysts.

The present paper describes an efficient, high-yielding approach for the immobilization of oxo-vanadium Schiff base on the polymer supports *via* covalent attachment with better catalyst loading using Staudinger ligation (Figure 1).

In the present study, azidomethyl-polystyrene and azidomethyl-MeOPEG$_{5000}$, easily accessible from commercially available Merrifield resin and MeO-PEG$_{5000}$, respectively, were employed as model supports. The immobilization of oxo-vanadium Schiff base **2** was carried out by using the Staudinger ligation coupling strategy as depicted in Scheme 1. The required oxo-vanadium Schiff base **2** was readily prepared by the two-step sequence involving condensation of salicylaldehyde with 4-aminobenzoic acid to

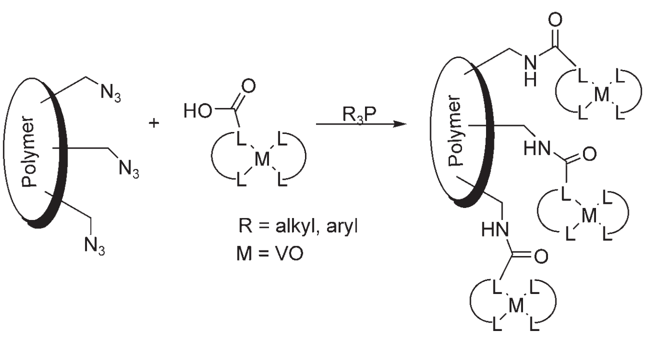
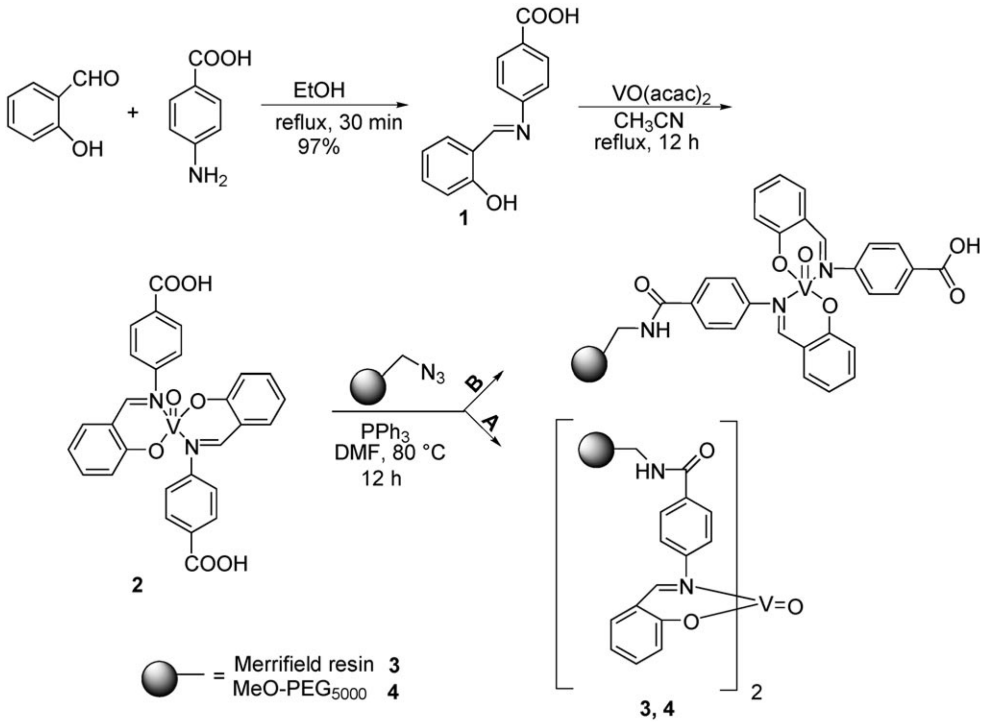


Figure 1. Formation of polymer bound oxo-vanadium Schiff base by Staudinger ligation.



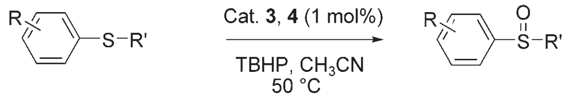
Scheme 1. Synthesis of immobilized oxo-vanadium Schiff base.

give Schiff base **1** followed by its reaction with vanadyl acetylacetonate in acetonitrile to yield oxo-vanadium Schiff base **2** in nearly quantitative yield. Reaction of the prepared oxo-vanadium Schiff base **2** with azidomethyl-polystyrene resin in the presence of an equivalent amount of triphenylphosphine in DMF at 80 °C resulted in covalently attached polystyrene-bound vanadyl Schiff base **3** as a brown solid in a virtually quantitative reaction as judged by the complete disappearance of typical azide band at 2095 cm^{-1} in the IR spectrum. The yield of **3** was calculated by the increased weight of resin.

The prepared polystyrene-bound complex **3** was characterized by IR, elemental and thermogravimetric analyses. The IR spectra showed bands at 1600 cm^{-1} due to C=N of Schiff base, 1667 cm^{-1} due to carbonyl band of amide, 3354 cm^{-1} due to NH of amide and a band at 981 cm^{-1} characteristic for V=O. The presence of an amide band at 1667 cm^{-1} and disappearance of the bands corresponding to C=O and OH of the carboxylic group revealed the covalent attachment of complex **2** with the polystyrene support at both the ends of the complex (Scheme 1, path A). However the possibility of covalent attachment of the complex with the polystyrene support at one end of the complex could not be ruled out completely (Scheme 1, path B). Elemental analysis and TGA data also supported the predominant attachment of polymer at both ends of the complex **2**. The amount of catalyst loaded onto the polystyrene resin was found to be 0.89 $\mathrm{mmol\,g}^{-1}$ as estimated from the nitrogen content determined by elemental analysis.[6]

The vanadium content of the prepared polymer-bound complex **3** was calculated by thermo gravimetric analysis (TGA) under an oxygen atmosphere. The catalyst was found to be stable thermally up to *ca.* 150 °C and there was weight loss in the temperature range 200–500 °C due to decomposition of part of the ligand moiety and the polystyrene structure. Sublimation of the left-over residue (7.5%) at 750 °C suggested the formation of V_2O_5 which revealed the percentage of vanadium in the prepared catalyst to be 4.2% (0.82 $\mathrm{mmol\,g}^{-1}$ of resin).

Similarly, the MeOPEG_{5000}-immobilized oxo-vanadium complex **4** was prepared by Staudinger ligation (Scheme 1). The required azido functionalized $\mathrm{MeO\text{-}PEG}_{5000}$ was prepared by the reaction of MeOPEG_{5000} with sodium azide in ethanol under reflux for 12 h. The PEG-immobilized oxo-vanadium complex **4** was separated from the reaction mixture by precipitation with diethyl ether, washed with 2-propanol, diethyl ether and dried under vacuum (yield: 92%). Again, the covalent attachment of complex **2** with MeOPEG_{5000} predominantly at both ends was confirmed by the presence of the 1667 cm^{-1} band and disappearance of the COOH band at 1715 cm^{-1} in the IR spectra (Scheme 1, path A). The amount of the catalyst loading onto the MeOPEG_{5000} support was found to be 0.07 $\mathrm{mmol\,g}^{-1}$,[7] as estimated from the nitrogen content determined by elemental analysis.



5 **6**

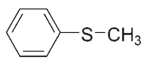
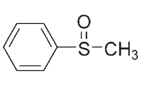
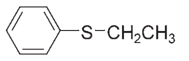
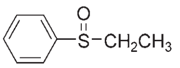
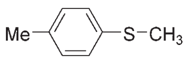
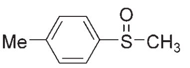
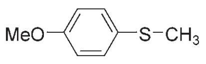
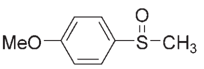
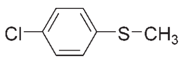
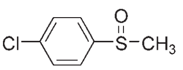
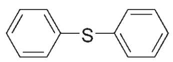
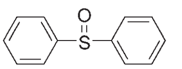
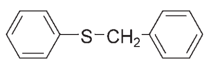
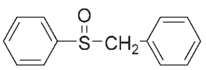
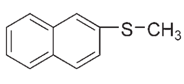
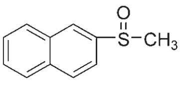
Scheme 2. Oxidation of sulfides using immobilized catalysts.

The catalytic activity of the prepared immobilized oxo-vanadium Schiff bases **3** and **4** and a comparison with the corresponding homogeneous oxo-vanadium Schiff base **2** was studied for the oxidation of sulfides **5** to the corresponding sulfoxides **6** using aqueous *tert*-butyl hydroproxide [TBHP] as oxidant (Scheme 2).

A variety of sulfides were selectively and efficiently oxidized to the corresponding sulfoxides in excellent yields by using aqueous TBHP as oxidant in the presence of immobilized catalysts (1 mol%) in acetonitrile at 50 °C. At the end of the reaction (monitored by TLC) the catalyst **3** was separated from the reaction mixture by simple filtration and catalyst **4** was recovered by precipitation with diethyl ether followed by filtration. The filtrate was subjected to usual work-up to give the corresponding sulfoxides. The results of these experiments are summarized in Table 1. The conversion and selectivity of the products were determined by ^{1}H NMR spectroscopy. We also compared the catalytic activity of the immobilized catalysts with the corresponding homogeneous oxo-vanadium Schiff base **2** by carrying out the oxidation of methyl phenyl sulfide under the described reaction conditions (Table 1, entry 1). Although catalytic efficiency of the immobilized Schiff base complexes **3** and **4** was found to be comparable with that of the oxo-vanadium Schiff base **2**, facile recovery as well as recycling ability of the immobilized complexes make them superior catalysts. Enhanced conversion as well as catalytic activity of polymer-anchored oxo-vanadium Schiff bases in comparison to their homogeneous analogues have previously been reported for the oxidation of styrene and ethylbenzene with H_2O_2.[2c]

Next, we checked the recyclability and reusability of immobilized catalysts **3** and **4** by using the methyl phenyl sulfide as a model substrate. At the end of the reaction the catalyst **3** recovered by simple filtration was washed with dichloromethane, dried and reused for subsequent experiments (four runs) by adding fresh substrate and oxidant under similar reaction conditions. Similarly, the catalyst **4**, recovered by precipitation with diethyl ether, was thoroughly washed, dried and reused as such for subsequent runs (four runs) under similar reaction conditions. In both cases reaction times and yield of the methyl phenyl sulfoxide remained almost same, establishing the recyclabil-

Table 1. Oxidation of sulfides to sulfoxides.[a]

Entry	Sulfide **5**	Product **6**	Catalyst	Time [h]	Selectivity [%][b]	Conversion/Yield[c]
1			**2**	1.0	100	100/96
2			**3**	1.5	100	100/96
3			**4**	1.0	100	100/97
4			**3**	1.5	100	100
5			**4**	1.25	10	100
6			**3**	1.0	100	100/97
7			**4**	1.0	100	100/95
8			**3**	2.5	100	80/74[d]
9			**4**	2.0	100	85/82[d]
10			**3**	2,75	100	90
11			**4**	2.5	100	94
12			**3**	3.0	100	100/96
13			**4**	3.0	100	100/96
14			**3**	2.75	100	100
15			**4**	2.75	100	100
16			**3**	2.5	60[e]	80
17			**4**	2.0	72[e]	85

[a] *Reaction conditions:* sulfide (1 mmol), aqueous TBHP (2.5 mmol), catalyst (1 mol%), acetonitrile (2 mL) at 50 °C.

[b] Conversion and selectivity determined by ^{1}H NMR.

[c] Isolated yields.

[d] Product was purified by column chromatography.

[e] Sulfones were obtained as side products.

Table 2. Results of recyclability experiments.[a]

Run	Catalyst **3**		Catalyst **4**	
	Time [h]	Conv.[b]/Yield[c]	Time [h]	Conv.[b]/Yield[c]
1	1.5	100/96	1.0	100/97
2	1.5	100/96	1.0	100/96
3	1.5	100/96	1.0	100/96
4	1.5	100/95	1.0	100/96

[a] *Reaction conditions:* methyl phenyl sulfide (1 mmol), aqueous TBHP (2.5 mmol), catalyst (1 mol%), CH_3CN (2 mL) at 50 °C.

[b] Conversion determined by ^{1}H NMR.

[c] Isolated yields.

ity and reusability of the immobilized oxo-vanadium Schiff bases **3** and **4** (Table 2). Additionally, we have carried out controlled experiments to check the recyclability of the immobilized catalysts in the oxidation of methyl phenyl sulfide by stopping the reaction after 30 min and analyzing the conversion to methyl phenyl sulfoxide by ^{1}H NMR. No significant difference in the conversions was observed while using fresh and recycled catalysts even after 3 runs.

To check the leaching, we stirred the immobilized catalysts **3** and **4** in acetonitrile at 50 °C for 3 h. The immobilized catalysts were removed and the filtrates thus obtained were used for the oxidation of methyl phenyl sulfide with aqueous TBHP as oxidant under the described reaction conditions. In both cases, no oxidation occurred even after prolonged reaction times (3 h). Selected filtrate samples during the recycling experiments were also analyzed by inductive coupled plasma atomic emission spectroscopy (ICP-AES) and no solvated vanadium could be detected (0.1 ppm detection limit), which established that there was no leaching and the reaction is truly heterogeneous in nature.

In summary, we have demonstrated the successful application of Staudinger ligation as an efficient and high-yielding approach for immobilizing the oxo-vanadium Schiff base onto polystyrene resin and $MEOPEG_{5000}$ *via* covalent attachment. The key advantages such as simplicity in use, versatility, high efficiency in terms of high catalyst loading onto polymer support without using excess of reagents or metal under mild reaction conditions, make this coupling strategy a facile and improved approach for the preparation of immobilized metal complexes. The prepared polymer-bound oxo-vanadium Schiff bases were found to be efficient catalysts for the selective oxidation of sulfides to sulfoxides using aqueous TBHP as oxidant. Both catalysts were recovered and reused for four runs without detectable leaching of metal and loss in catalytic activity.

Experimental Section

Schiff Base 1

To a stirred solution of 4-aminobenzoic acid (6.85 g, 0.05 mol) in ethanol (150 mL) was added salicylaldehyde (6.10 g, 0.05 mol), triethylamine (10.10 g, 0.1 mol) and the resulting mixture was stirred at room temperature for 30 min. The precipitated yellow Schiff base was separated from the reaction mixture by filtration and recrystallized with methanol to afford ; yield: 11.68 g (97%). IR: ν=3430, 3062, 2852, 1680, 1610, 1594 cm^{-1}; ^{1}H NMR (300 Hz, $CDCl_3$): δ=6.97–7.02 (m, 2H), 7.42–7.49 (m, 3H), 7.70 (d, 1H, J=7.68 Hz), 8.01 (d, 2H, J=8.51 Hz), 9.00 (s, 1H), 12.45 (s, 1H), 13.85 (s, 1H); ^{13}C NMR (300 Hz, $CDCl_3$): δ=116, 120.6, 122.5, 135.5, 158.0, 162.2, 169.4; MS: m/z =242 (MH^+); anal. calcd. (found) % for **1**: C 69.70 (69.83), H 4.56 (4.67), N 5.80 (5.78).

Oxo-Vanadium Schiff Base 2

To a stirred solution of Schiff base **1** (2.41 g, 10 mmol) in dry acetonitrile (20 mL) was added vanadyl acetylacetonate (1.33 g, 5 mmol) and the resulting mixture was refluxed for 12 h under a nitrogen atmosphere. The precipitated green solid was filtered off and washed thoroughly by acetonitrile, diethyl ether and dry under vacuum; yield: 2.59 g (95%); MS: m/z=548 (M+1); IR: ν=3365, 3065, 1660, 1600, 1521, 981 cm^{-1}; anal. calcd. (found) % for **2**: C 63.21 (62.69), H 4.96 (4.90), N 5.27 (5.33).

Polystyrene Immobilized Oxo-Vanadium Schiff Base 3

A mixture containing azidomethyl-polystyrene resin[8] (1.0 g, 4.2 mmol N_3/g), triphenylphosphine (1.17 g, 4.5 mmol) and oxo-vanadium Schiff base **2** (1.15 g, 2.1 mmol) in dry DMF (25 mL) was heated at 80 °C for 12 h. The brown-colored precipitate was separated by filtration and washed thoroughly with DMF, hot methanol and dried under vacuum to afford **3**; 1.80 g (92%). IR: ν=3351, 2922, 1667, 1600, 1547, 971 cm^{-1}; anal. calcd. for nitrogen: 5.99% (found: 4.99%)

$MeOPEG_{5000}$-Immobilized Oxo-Vanadium Schiff Base 4

A mixture containing azidomethyl-$MeOPEG_{5000}$ (20 g, 4 mmol), triphenylphosphine (1.17 g, 4.5 mmol) and oxo-vanadium Schiff base **2** (1.10 g, 2.0 mmol) in dry DMF (30 mL) was heated at 80 °C for 12 h. The reaction mixture was concentrated under reduced pressure and the polymer was separated from the reaction mixture by precipitation with diethyl ether, washed with 2-propanol, diethyl ether and dried under vacuum to yield dark brown-colored PEG-supported catalyst **4**; yield: 19.41 g (92%). IR: n=3260, 2879, 1676, 1605, 1466, 960 cm^{-1}; anal. calcd. for nitrogen: 0.53% (found: 0.39%).

General Experimental Procedure for Oxidation of Sulfides using TBHP as Oxidant

Into a stirred mixture of sulfide (1 mmol), aqueous 70% TBHP (2.5 mmol) in acetonitrile (3 mL) was added polymer-bound catalyst (1 mol%). The resulting mixture was heated at 50 °C for the time reported in the Table 1. Completion of the reaction was analyzed by TLC. After completion of the reaction, the catalyst was separated by filtration or by precipitation with diethyl ether followed by filtration and reused as such for subsequent experiments. The filtrate so obtained was concentrated under reduced pressure and dissolved in dichloromethane (10 mL). The organic layer was washed with water (2×15 mL), dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to give corresponding oxidized product. The conversion of sulfides to sulfoxides and selectivity were determined by ^1H NMR.

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[6] Starting from the 4.2 mmol g^{-1} polystyrene resin, the theoretical loading of the complex **2** should be 1.01 mmol complex/g of resin.

[7] Theoretical loading of the **2** onto PEG_{5000} should be 0.09 mmol/g of polymer.

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