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Molybdenum liquid salts immobilized on ionic liquid-modified silica as efficient heterogeneous catalysts for sulfoxide reduction

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ABSTRACT

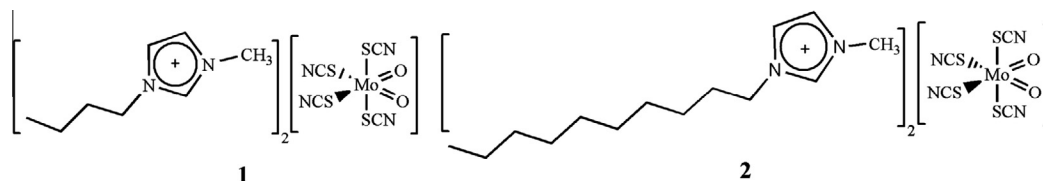
Two room temperature liquid salts containing molybdenum(VI), [BMIM]₂[MoO₂(NCS)₄] (**1**) and [DMIM]₂[MoO₂(NCS)₄] (**2**), were immobilized on ionic liquid-modified silica leading to materials which showed notable catalytic activity for the reduction of sulfoxides into sulfides with triphenylphosphine (PPh₃). The molybdenum liquid salts immobilized on the supported ionic liquid phase could be reused at least for three catalytic cycles without significant loss of activity.

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Catalytic reactions using ionic liquids (ILs) as bulk solvents usually present advantages of high catalytic activity and good selectivity.¹ Nevertheless, using ILs as bulk solvents in conventional biphasic catalysis normally needs a large amount of ILs that are still considered as expensive solvents. In addition, the high viscosity of ILs often causes mass transfer limitations. Thus, a large proportion of the catalytically active species is not able to take part in the catalytic process. The concept of supported ionic liquid phase (SILP) catalysis was introduced by immobilization of transition metal catalysts immersed in a thin film of ionic liquid on a solid support by Mehnert et al.² Dissolving catalytic species in a supported film of ionic liquid was introduced as a promising strategy for immobilizing catalysts.³ The ionic liquid layer acts as a phase for the catalytic reaction combining both the advantages of an ionic liquid and heterogeneous catalytic systems.⁴ Various catalytic reactions such as Friedel–Crafts,⁵ Rh-catalyzed hydroformylations,⁶

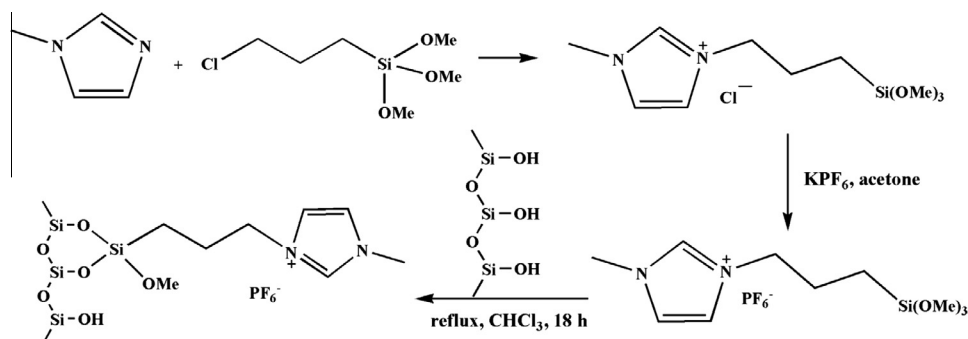
hydrogenations,⁷ Ru-catalyzed ring-closing olefin metathesis,⁸ and Pd-catalyzed carbon–carbon coupling reactions⁹ have been reported using supported ionic liquid phase catalysis.

Despite various studies on molybdenum catalysts in ionic liquids,¹⁰ there are only a few reports on molybdenum catalysts immobilized in supported ionic liquids.¹¹ Among various oxomolybdenum(VI) compounds studied extensively as catalysts for oxygen atom transfer, [MoO₂(NCS)₄]²⁻ has been reported as a simple active oxo-transfer catalyst or efficient oxidizing agent.¹² In continuation of our studies on molybdenum compounds as catalysts,¹³ we previously reported the synthesis and catalytic applications of several new ionic liquids containing the [MoO₂(NCS)₄]²⁻ anion for the deoxygenation of sulfoxides in an ionic liquid/organic biphasic system.¹⁴ In the present work, the immobilization of [BMIM]₂[MoO₂(NCS)₄] (**1**) (BMIM = 1-butyl-3-methylimidazolium) and [DMIM]₂[MoO₂(NCS)₄] (**2**) (DMIM = 1-*n*-decyl-3-methylimida-



Scheme 1. [BMIM]₂[MoO₂(NCS)₄] (**1**) and [DMIM]₂[MoO₂(NCS)₄] (**2**) as molybdenum containing ionic liquids.

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Scheme 2. Synthesis of the ionic liquid-modified silica.

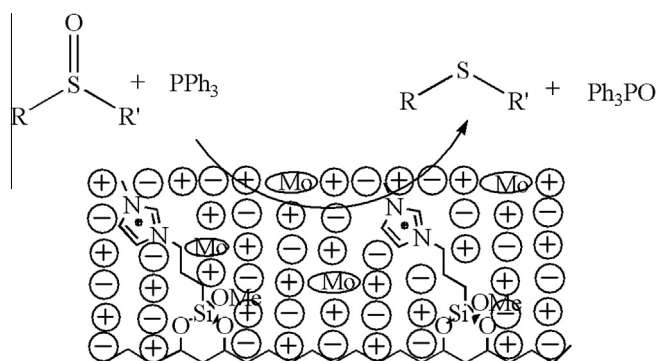
zolium) (Scheme 1) on ionic liquid-modified silica is reported. Both molybdenum based supported catalysts proved to be efficient for oxo-transfer reactions.

The preparation of the ionic liquid-modified silica is shown in Scheme 2. 1-Methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride was synthesized by the reaction of (3-chloropropyl)trimethoxysilane and 1-methylimidazole (see Supplementary data).¹⁵ The obtained ionic liquid was treated with potassium hexafluorophosphate in acetone to give 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hexafluorophosphate. Next, dried silica gel (with a surface area of 550 m²/g and particle size of 230–400 mesh) was heated with 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hexafluorophosphate in refluxing chloroform to give the modified support materials.^{2,11} Elemental analysis (C and N quantification) showed that 0.714 mmol of 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hexafluorophosphate ionic liquid was anchored to 1.0 g silica. Comparing the IR spectrum of bare silica with that of silica modified with 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hexafluorophosphate confirmed the presence of the ionic liquid anchored to the silica surface (Fig. S1). The bands around 1100 cm⁻¹ and 1635 cm⁻¹ are associated with the stretching of the siloxane bonds (≡Si–O) on the silica and bending of the water molecules, respectively. The broad band at 3430 cm⁻¹ is due to stretching of the O–H bonds of the silanols and water molecules in silica. The IR spectrum of silica modified with the ionic liquid additionally showed a band at 1575 cm⁻¹ due to the aromatic C=C stretching of the imidazolium ring and the C–H stretching vibration of imidazolium at 3180 cm⁻¹ which demonstrated that the ionic liquid had been attached to silica. [BMIM]₂[MoO₂(NCS)₄] (**1**) and [DMIM]₂[MoO₂(NCS)₄] (**2**) were synthesized as previously reported.^{12c,14} Molybdenum complexes were immobilized into the ionic liquid layer on the surface of ionic liquid-modified silica by adding [BMIM][PF₆] as second ionic liquid

to obtain the catalysts Mo1/SILP and Mo2/SILP.¹⁶ The loading of molybdenum in Mo1/SILP and Mo2/SILP was shown to be 0.064 and 0.057 mmol/g, respectively, according to inductively coupled plasma-atomic emission spectroscopy. The color of both molybdenum supported catalysts was orange-red before taking part in oxo-transfer catalytic process.

The reduction of sulfoxides using Mo1/SILP and Mo2/SILP as catalysts was performed as shown in Scheme 3.¹⁷ The conversion increased remarkably on raising the temperature from room temperature to 50 °C, using methyl phenyl sulfoxide as model substrate (Table 1). The catalyst amount, referenced to the number of mmols of the supported molybdenum complex, was changed in the range of 0–5 mol % (Fig. S2). In the absence of catalyst and under the same reaction conditions, the conversion of methyl phenyl sulfoxide was negligible. Sulfoxide conversion increased to 87% with an increase in the catalyst amount to 2.5 mol %. Further increasing the catalyst amount did not cause a significant enhancement in the conversion. Comparing this SILP catalysis with a biphasic catalytic system using [BMIM]₂[MoO₂(NCS)₄] as catalytic species,¹⁴ it was observed that the mol % of the molybdenum catalyst required for catalytic reduction was reduced by 50% in this SILP catalysis. This can be explained by the fact that a large part of the catalytic species remains in the bulk ionic liquid phase in biphasic systems, which cannot take part in the catalytic process. It seems that immobilizing the molybdenum salts into the ionic liquid layer on the surface of silica decreased the amount of molybdenum catalyst required for the reaction. This catalytic system was used for reducing other sulfoxide substrates, that is, diethyl sulfoxide and diphenyl sulfoxide, into their corresponding sulfides. It was observed that the Mo1/SILP catalyst was also an efficient catalyst for oxo-transfer from these sulfoxide substrates to PPh₃ (Table 2).

The recyclability of Mo1/SILP and Mo2/SILP was investigated in the reduction of methyl phenyl sulfoxide in the presence of PPh₃ (Table 3). After each catalytic cycle, the separated catalyst was re-



Scheme 3. Reduction of sulfoxides by molybdenum supported ionic liquid phase catalysts.

Table 1 The effect of the temperature on the catalytic reduction of methyl phenyl sulfoxide by molybdenum ionic liquid supported phase catalysts^a

Entry	Catalyst	Temperature	Conversion ^b (%)
1	–	RT	0
		50 °C	0
2	Mo1/SILP	RT	40
		50 °C	87
3	Mo2/SILP	RT	30
		50 °C	85

^a Reaction conditions: solvent: toluene (1 ml), catalyst/methyl phenyl sulfoxide/PPh₃ ratio = 1:40:40.

^b Conversion (%) determined by GC after 28 h using chlorobenzene as the internal standard.

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