

Oxidative carbonylation of aniline with a mesoporous silica gel immobilised Se-functionalised ionic liquid catalyst

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A series of BMImBF₄-templated mesoporous silica gel immobilised Se-functionalised ionic liquids have been prepared. The catalysts were characterised by BET, FTIR and ICP-AES, and the results showed that the content of Se increased from 2.7 to 4.76 wt% with pore volume increasing from 0.83 to 1.26 cm³ g⁻¹. Preliminary tests of this catalyst system on the carbonylation of aniline to afford methyl phenyl carbamate (MPC) indicated that good catalytic activity (higher than 74% aniline conversion with 99% MPC selectivity) could be achieved with higher than 150 mol h⁻¹ mol⁻¹ turnover frequency (TOF). TOF and aniline conversion slightly increased with increasing the content of Se from 2.7 to 3.0 wt%, then decreased when the content of Se increased to more than 3.0 wt%, this suggested that 2.7 to 3.0 wt% Se content should be appropriate for MPC synthesis. The appropriate Se content could be obtained by adjusting the range of pore volume of mesoporous silica gel from 0.83 to 0.85 cm³ g⁻¹. In addition, the recycling test indicated that there was almost no deactivation of the catalyst when it was reused four times.

Keywords: silica gel, ionic liquids, selenium, non-phosgene, methyl phenyl carbamate

Isocyanates are currently manufactured by the phosgenation of the corresponding amine with toxic phosgene. This usually causes serious environmental pollution and equipment corrosion. As the key intermediates of phosgene-free synthesis of isocyanates, carbamates have been extensively studied in the past two decades. An important approach is the reductive carbonylation of nitro compounds using transition metal complexes as the catalyst.^{1–4} The methoxycarbonylation of amines in the presence of dimethyl carbonate (DMC) has also been reported.^{5,6} The deactivation of the noble metal catalysts is one of the main problems in reductive carbonylation, while the price of DMC inhibits its large-scale use in methoxycarbonylation. Besides the reductive carbonylation and methoxycarbonylation methods, the oxidative carbonylation of amines has also been investigated extensively.^{7–13} However, the recovery of the noble-metal catalysts was difficult. It has been reported that selenium compounds and ionic liquids containing anionic selenium species could be used for the oxidative carbonylation of amines.^{14–18} This should be a good choice for the development of an economic and recoverable noble-metal free catalyst system for the oxidative carbonylation of aniline.

Mesoporous silica materials with different structures have attracted widespread attention due to their potential applications in catalysis, biosensors, chromatographic separation, microelectronic and optoelectronic technologies.^{19–21} Recently, ionic liquids were reported to be effective templates for preparing mesostructured materials.²² This may offer new opportunities for catalyst preparation using mesoporous silica gel (prepared with ionic liquids as the template) as a support or catalyst.

Herein, a series of Se-IL-SiO₂ catalysts were prepared. According to ref 14 and our research experience, aniline and methanol easily form a carbamate, so these were selected as the reactants to test the Se-IL-SiO₂ catalysts (Scheme 1).

Results and discussion

Mesoporous silica gel, prepared with various amounts of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate

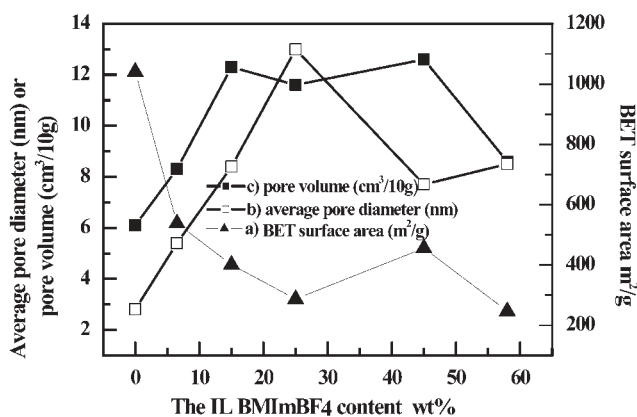
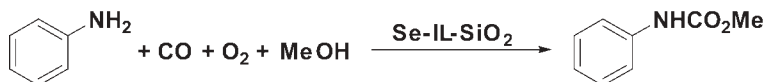


Fig. 1 The relationship between the pore structure and the amounts of BMImBF₄: (a) BET surface area, (b) pore volume, and (c) pore diameter.

(BMImBF₄) as the template, were examined, Fig. 1. It can be seen that the BET surface areas decreased from ~1041 to ~250 m² g⁻¹, pore volumes and average pore sizes increased from 0.61 to 1.26 cm³ g⁻¹ and 2.8 nm to 13 nm respectively when the amount of ionic liquid was increased from 0 to 58 wt%. These data suggested that all SiO₂ used in this work was mesoporous silica gel.

The content of selenium for 14.7 wt% Se-IL-SiO₂-6.5 was 2.70 wt%, for 25.1 wt% Se-IL-SiO₂-15 was 4.65 wt%, for 23.9 wt% Se-IL-SiO₂-25 was 4.42 wt%, for 25.7 wt% Se-IL-SiO₂-45 was 4.76 wt%, and for 16.2 wt% Se-IL-SiO₂-58 was 3.0 wt% (the numbers 6.5, 15, 25, 45 and 58 indicate the use of 6.5 wt%, 15 wt%, 25 wt%, 45 wt% and 58 wt% BMImBF₄ as the template).

From the FT-IR spectra of Se-IL and Se-IL-SiO₂ (Fig. 2), two characteristic peaks (1469 and 1571 cm⁻¹) were observed: the first ascribed to the in-plane C-H deformation vibration, and the C-C and C-N stretching vibrations of the imidazole



Scheme 1 MPC synthesis via the oxidative carbonylation of aniline.

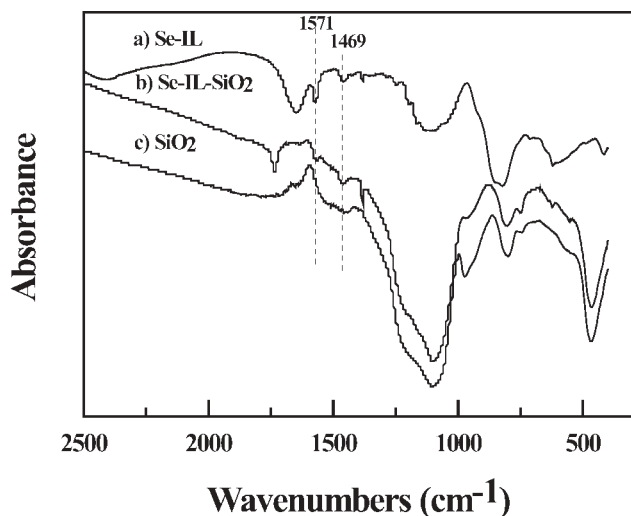


Fig. 2 FT-IR spectra of (a)Se-IL; (b) Se-IL-SiO₂; and (c)SiO₂.

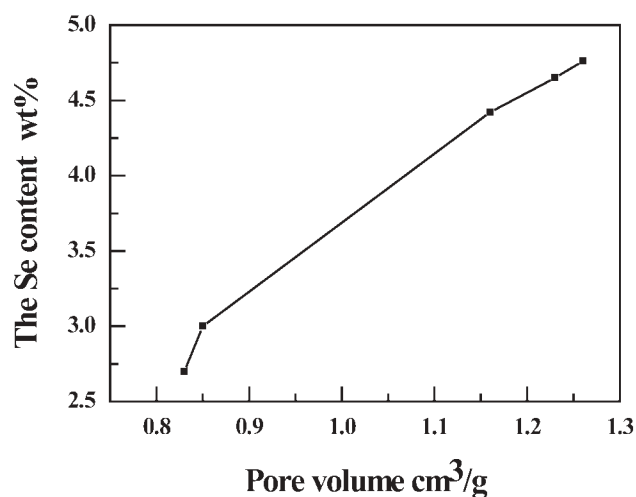


Fig. 3 The relationship between the Se content and pore volume of mesoporous silica gel.

ring;²⁵ the second to the CH₃ bending vibration. This suggests that Se-IL were anchored on the SiO₂.

As shown in Fig. 3, it can be seen that the content of Se in the catalysts increased from 2.7 wt% to 4.76 wt% as the pore volume of the mesoporous silica gel increased from 0.83 to 1.26 cm³ g⁻¹. It seems that there is a close relationship between the Se content and the structure of mesoporous silica gel.

As shown in Table 1, 74%, 94%, 92%, 88%, 84% aniline conversions with more than 99% methyl phenyl carbamate

Table 1 The results of oxidative carbonylation of aniline to methyl phenyl carbamate

Entry	Catalyst	Conversion %	Selectivity %	TOF /mol h ⁻¹ mol ^{-1c}
1	14.7 wt% Se-IL-SiO ₂ -6.5	74	>99	232
2	25.1 wt% Se-IL-SiO ₂ -15	92	>99	168
3	23.9 wt% Se-IL-SiO ₂ -25	94	>99	181
4	25.7 wt% Se-IL-SiO ₂ -45	88	>99	157
5	16.2 wt% Se-IL-SiO ₂ -58	84	>99	238
6	16.2 wt% Se-IL-SiO ₂ -58 ^a	75	>99	425
7	16.2 wt% Se-IL-SiO ₂ -58 ^b	82	>99	235

Aniline (0.5 mL), catalyst (50 mg), methanol (5 mL), P = 5 MPa (CO/O₂ = 9/1 V/V), t = 1 h, T = 393 K; ^a1 mL aniline; ^bthe catalyst was reused for the 4th time, ^cTOF = mol substrate converted h⁻¹ mol⁻¹ Se.

(MPC) selectivity, and 232, 168, 181, 157, 238 mol h⁻¹ mol⁻¹ TOF were obtained with 14.7 wt% Se-IL-SiO₂-6.5, 25.1 wt% Se-IL-SiO₂-15, 23.9 wt% Se-IL-SiO₂-25, 25.7 wt% Se-IL-SiO₂-45, and 16.2 wt% Se-IL-SiO₂-58 as the catalysts, respectively (entries 1–5). These results suggested that the Se-IL-SiO₂ catalyst system had a high catalytic activity. TOFs of all catalysts in this work exceeded 150 mol h⁻¹ mol⁻¹. Note that TOFs for the selenium-based catalyst system reported by other groups are usually lower than 100 mol h⁻¹ mol⁻¹.^{26–29} It should also be mentioned that TOFs for Se-functionalised ILs catalyst systems reported by other groups are usually lower than 180 mol h⁻¹ mol⁻¹ when aniline conversion was higher than 70%.¹⁴

Since the TOF was higher than those of the selenium-based catalyst systems and the Se-functionalised IL catalysts systems reported by other groups, and the 16.2 wt% Se-IL-SiO₂-58 catalyst showed the highest TOF, MPC synthesis was investigated in detail with the latter as the representative catalyst.

The results of 16.2 wt% Se-IL-SiO₂-58 catalysed aniline carbonylation are listed in Table 1. The conversion of aniline decreased from 84% to 75%, while TOF increased from 238 to 425 mol h⁻¹ mol⁻¹ (entries 5 and 6) when the aniline/methanol molar ratio was doubled. These results suggest that the molar ratio of aniline/methanol has an important impact on MPC synthesis.

The reuse of the catalyst was also investigated. To our delight, 82% aniline conversion with 99% MPC selectivity and 235 mol h⁻¹ mol⁻¹ TOF were obtained when the catalyst was reused for the 4th time (entry 7). Almost the same aniline conversion, MPC selectivity and TOF were achieved, which suggests that the catalyst was stable enough for reuse.

As shown in Fig. 4, the aniline conversion increased from 74 to 94% when the content of Se increased from 2.7 to 4.42 wt%, then decreased from 94 to 88% with further increasing of the content of Se from 4.42 to 4.76 wt%, while the TOF increased slightly from 232 to 238 mol h⁻¹ mol⁻¹ with the increasing of the content of Se from 2.7 to 3.0 wt%. The TOF then decreased from 238 to 157 mol h⁻¹ mol⁻¹ when the content of Se increased from 3.0 to 4.76 wt%. These results suggest that 2.7–3.0 wt% Se should be appropriate for MPC synthesis. As mentioned above, the content of Se increased with the increasing of the pore volume of mesoporous silica gel. Therefore, the appropriate content of Se for higher catalytic activity on MPC synthesis could be obtained by adjusting the pore volume of mesoporous silica gel.

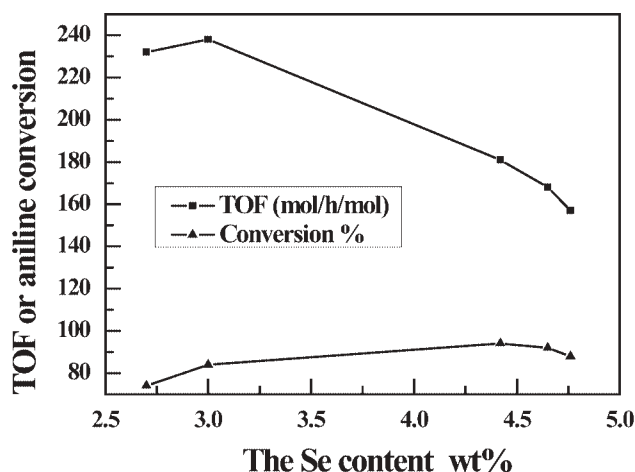


Fig. 4 The relationship between TOF and the aniline conversion to the Se content.

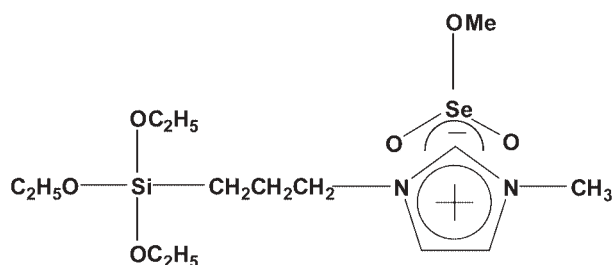
In summary, a series of Se-IL-SiO₂ was prepared and members used as highly efficient catalysts for the oxidative carbonylation of aniline. Higher than 74% aniline conversion with 99% MPC selectivity and up to 425 mol h⁻¹ mol⁻¹ TOF could be obtained. There was no obvious deactivation of the catalyst when the catalyst was reused four times. More importantly, the catalytic capability could be effectively regulated by adjusting the pore volume of mesoporous silica gel.

Experimental

CAUTION: Because of the toxic and irritant properties of Se compounds, their handling and the catalyst preparation and use should be carried out in a fume cupboard with appropriate precautions.

Selenium dioxide (98.0%), K₂CO₃ (99.0%), hydrochloric acid (36–38 wt%), Cl(CH₂)₃Si(OEt)₃, methylimidazole, aniline and methanol were all analytical reagent grade and used as received. Carbon monoxide (99.99%), and oxygen (99.99%) were used as purchased.

BMImBF₄, RMImSeO₂(OCH₃) (Se-IL) (BMIm = 1-butyl-3-methylimidazolium, RMIm = 1-Si(OEt)₃(CH₂)₃-3-methylimidazolium) and KSeO₂(OCH₃) were synthesised respectively according to previously published papers with slight modifications,^{14,23} replacing Cl(CH₂)₃CH₃ with Cl(CH₂)₃Si(OEt)₃. The structural formula of Se-IL in this work is shown in Scheme 2.



Scheme 2 The structure formula of Se-IL.

BMImBF₄-templated mesoporous silica gel was prepared as follows:²⁴ a mixture of tetraethoxyorthosilicate (TEOS, 10 mL, 45 mmol), EtOH (7 mL) and BMImBF₄ (0.2–4.0 g, 1.2–24 mmol) were heated to 60 °C. Then, hydrochloric acid (5 M, 5 mL) was added and the mixture coagulated. After ageing at 60 °C for 12 h, the solid material was dried under reduced pressure at 150 °C for 3 h, and 3–7 g solid samples were obtained. In order to obtain pure mesoporous silica gel or mesoporous silica gel skeleton, the samples were washed with ethanol under vigorous refluxing for 10 h when all BMImBF₄ should be washed out (tested by elemental analysis), and BMImBF₄-templated mesoporous silica gel with different structures was achieved. The samples were denoted as SiO₂-6.5 (6.5 was 6.5 wt% BMImBF₄ as the template), SiO₂-15, SiO₂-25, SiO₂-45 and SiO₂-58.

Se-IL-SiO₂ was prepared as follows: in a typical procedure, HCl solution (10 mL 10 M) was mixed with SiO₂-6.5 (1 g) and stirred for 12 h at room temperature. It was then filtered off and washed with

toluene (50 mL) and ethanol (150 mL) sequentially, and dried at 80 °C for 12 h. The pretreated SiO₂-6.5 (1 g), toluene (20 mL) and Se-IL (3 g) were introduced into a conical flask and refluxed at 110 °C for 24 h. After being filtered off, washed with toluene (50 mL) and ethanol (150 mL) sequentially and dried at 80 °C for 12 h, the catalyst was denoted as 14.7 wt% Se-IL-SiO₂-6.5 (14.7 wt% was the content of Se-IL) (Scheme 3). The same procedure was used for the preparation of other Se-IL-SiO₂ catalysts, *i.e.* 25.1 wt% Se-IL-SiO₂-15, 23.9 wt% Se-IL-SiO₂-25, 25.7 wt% Se-IL-SiO₂-45 and 16.2 wt% Se-IL-SiO₂-58.

The BET surface area, porous volume, and average pore diameter of SiO₂ in this work were measured by physisorption of N₂ at 76 K using a Micromeritics ASAP 2010 instrument. Before the measurement, the samples were degassed at 200 °C for 12 h, to remove moisture and adsorbed gases from the catalyst surface. The isotherms were elaborated according to the BET method for surface area calculation, with the Horwarth–Kavazoe and BJH methods used for micropore and mesopore evaluation, respectively.

The Se content of the catalysts was determined on an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Thermo-Elemental Company in the USA) after the samples were dissolved in aqueous nitric acid (5 M).

Fourier transform IR (FT-IR) spectra were recorded on a Nicolet FTIR 5700 spectrophotometer using the KBr pellet technique. The spectra were acquired by accumulating 64 scans at a resolution of 2 cm⁻¹ in the range of 400–4000 cm⁻¹.

All reactions were conducted in a 90 mL autoclave in a glass tube. In each reaction, 50 mg Se-IL-SiO₂ catalyst, 0.5 mL (or 1 mL) aniline, 5 mL methanol, and 5.0 MPa of mixture gases (CO purity 99.99%, 4.5 MPa and O₂ 99.99%, 0.5 MPa) were successively introduced without any additional organic solvent. All reactions proceeded at 393 K for 1 h. Qualitative analysis was conducted with an HP 6890/5793 GC-MS. Quantitative analysis was conducted over an Agilent 6820 GC, the conversion and selectivities were determined by an external standard, and were calculated according to the chromatographic peak areas of the resulting products given by the GC chemstation.

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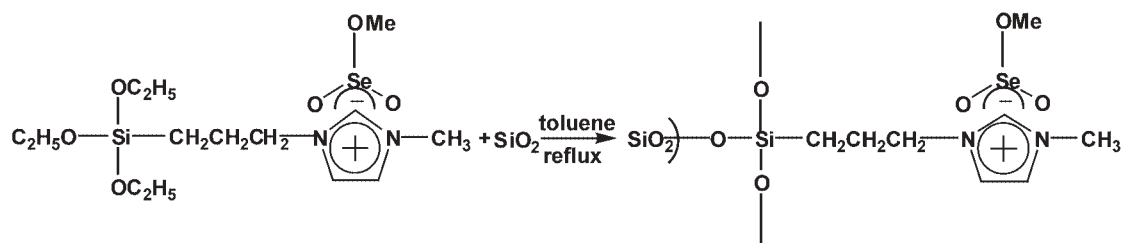
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Scheme 3 The process for preparation of Se-IL-SiO₂.

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