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Catalysis Today 105 (2005) 605–611

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Development of an immobilization method by encapsulating inorganic metal salts forming hollow microcapsules

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Abstract

In the present paper, a facile and cost effective method was developed to fabricate micrometer-sized hollow polyurea microcapsule via W/O emulsion, with the inorganic metal salts as encapsulated materials. The size of porosities and non-porous parts were uniform with diameter ranging from 20 to 40 nm for both interior and exterior surfaces. The immobilized nickel nanoparticle was well dispersed with diameter under 30 nm. Polyurea hollow microcapsules encapsulated with $NiCl_2$ presented better thermal stability than polyurea itself. The immobilization of $NiCl_2$ was rather effective, and no leaching could be observed under ethanol, toluene and water at 110 °C while stirring for 5 h. This heterogeneous microcapsule with $NiCl_2$ could be reused for benzaldehyde reduction with no loss of activity or selectivity, meaning that it is an effective immobilization method.

Keywords: Microencapsulation; Hollow microcapsule; Polyurea; Inorganic metal salts; Heterogeneous catalyst; Reduction

1. Introduction

Entrapment provides a method for immobilization, and it can control the release of active ingredients, sustain the effectiveness of ingredients, permit liquids to be handled as solids, protect reactive components until the time of use, allow the safe handling of toxic materials, and overcome product incompatibilities. Therein, microencapsulation, one of the entrapment methods to encapsulate materials in a polymeric coating, has recently been demonstrated to be a useful alternative strategy for reagent immobilization [1–3].

Since polyurea microcapsules are completely insoluble in water and other common solvents, and can incorporate both hydrophobic and hydrophilic active materials, they have gathered much focus as an effective method to prepare immobilized catalyst. Polyurea microcapsules are prepared by an in situ interfacial polymerization approach, which involves the dispersion of a solution of isocyanates and the reagent to be encapsulated in a suitable organic solvent into an aqueous mixture containing surfactants.

It has been demonstrated that metal species, such as $Pd(OAc)_2$ [4] can be encapsulated in polyurea and used as recoverable and reusable catalysts for alkenes hydrogenation [5], ketones hydrogenation [6], cross-coupling reaction [7], and hydrogenolysis of epoxides [8]. OsO_4 was also reported as a core material encapsulated in polyurea and has been effectively used as recoverable and reusable catalysts in dihydroxylation of olefins [9].

It should be mentioned that the reported polyurea encapsulated with Pd or Os compounds originated from an in situ interfacial polymerization via oil-in-water emulsion, i.e., the reagent to be encapsulated should be dissolved in an organic solvent first. For the smooth dispersion, valuable polymers, such as polymethylene polyphenylene diisocyanate and polyoxypropylene polyoxyethylene ether were necessary. This is not suitable for those cheap inorganic metal salts, which could only dissolve in water phase, making this method much limited and more expensive. Here, an in situ interfacial polymerization via water-in-oil emulsion with the inorganic metal salts to be encapsulated dissolved in water phase firstly, is reported; and after the occurrence of polymerization at the oil-water interface, the inorganic metal salts could be easily

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doi:10.1016/j.cattod.2005.06.006

encapsulated inside the microcapsules. Hollow microcapsules with inorganic metal salts on the interior surface could be obtained simply by drying to remove the water inside the microcapsules. As the core materials need to be dissolved in water phase instead of organic one, this method extends the variety of metal salts owing to the easily obtained water miscible metal salts.

2. Experimental

2.1. Sample preparation

The key to the successful synthesis of hollow microcapsule is in controlling the polymerization speed. The addition of inorganic metal salts, such as $NiCl_2$ lowered the reaction rate in comparison with that without inorganic metal salts cores, and different inorganic metal salts presented different reaction rates till the completion of interfacial polymerization. The urea group could be produced by the reaction between water and toluene 2,4-diisocyanate (abbreviated as 2,4-TDI) occurring at the oil–water interface, and unstable $–NCOOH_2$ was prepared and could be easily changed to $–NH_2$ group by the release of CO_2. The resultant TDI-based water-borne amine produced urea, i.e., –NHCONH– by the reaction with another 2,4-TDI. This subsequent reaction produced a polymer wall membrane onto the emulsion globules. Following this, the sample was washed and heated, the water inside the microcapsule was vaporized and thus the formation of hollow microcapsule with $NiCl_2$ dotted in the interior surface. Scheme 1 gives the complete process diagrammatically.

2.2. Characterization methods

The content of encapsulated inorganic metal was determined by a Z-5000 type atomic absorption spectrometry (AAS) manufactured by Hitachi Co. (Japan), with the detect limit for Ni element less than 0.2 ppm and analytical error less than 5%.

IR spectra were obtained using a Bruker EQUINOX 55 Fourier transform infrared spectrometer.

Scanning electron microscope (SEM) was performed using a LEO 1530 VP (German) with an Inca 300 EDAX attachment (Oxford Co., England).

High-resolution transmission electron microscopy (HRTEM) analysis was carried out using a Philips CM300 FEGTEM microscope operated at an accelerating voltage of 200 kV with the resolution of 0.2 nm. The specimens were prepared by ultrasonic dispersion in ethanol, evaporating a drop of the resultant suspension onto a holey carbon support grid.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) curves were measured with STA449C Jupiter analysers (NETZSCH Gerätebau GmbH). The samples were heated under inert nitrogen atmosphere with a rate of 10 °C/min.

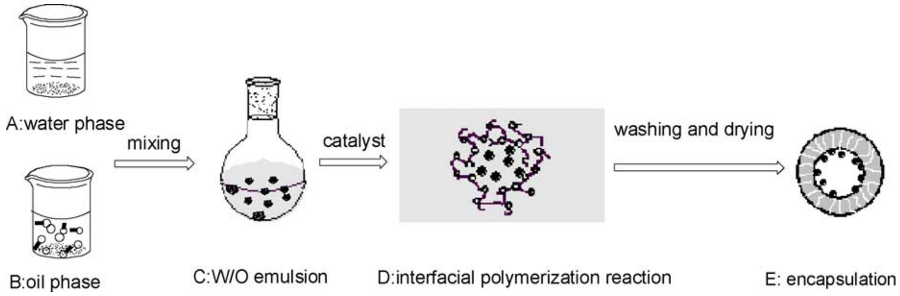
3. Results and discussion

3.1. Evidence for forming polyurea

In order to determine the polyurea structure of obtained microcapsules, FT-IR spectra were performed for the samples, such as pure 2,4-TDI and polyurea with encapsulated $NiCl_2$, as shown in Fig. 1.

The polyurea with encapsulated $NiCl_2$ had strong bands known for hydrogen bonded N–H stretching vibration at 3305 cm^{-1}. C–H stretching vibrations of methyl group were shown at 2925 and 2854 cm^{-1}. By the reaction of 2,4-TDI and water, NCO peak in diisocyanates at 2275 cm^{-1} disappeared and hydrogen bonded urea carbonyl was observed at 1654 cm^{-1}. These observed FT-IR spectra indicated the completion of reaction between 2,4-TDI and water, and the polyurea formation for microcapsule wall [10].

The energy dispersive X-ray (EDX) spectrum confirmed that the hollow microcapsules were composed of Ni and Cl. Also, carbon, nitrogen and oxygen were found in the EDX



Scheme 1. Schematic illustration of forming hollow microcapsule with $NiCl_2$ dotted in the interior surface (A) $NiCl_2$ was well dissolved in the deioned water forming homogeneous water phase. (B) 2,4-TDI and surfactant were well dissolved in cyclohexane forming homogeneous oil phase. (C) Water phase containing $NiCl_2$ was well dispersed in oil phase forming W/O emulsion. (D) Catalyst (triethylamine) was added into the above emulsion to promote the formation of polyurea microcapsules by interfacial polymerization between 2,4-TDI and water occurring at the oil–water interface, with the $NiCl_2$ aqueous solution encapsulated inside the microcapsules. (E) On washing and heating at 110 °C for 12 h, the $NiCl_2$ aqueous solution cores were vaporized, leaving $NiCl_2$ dotted in the interior surface, thus forming hollow microcapsules.

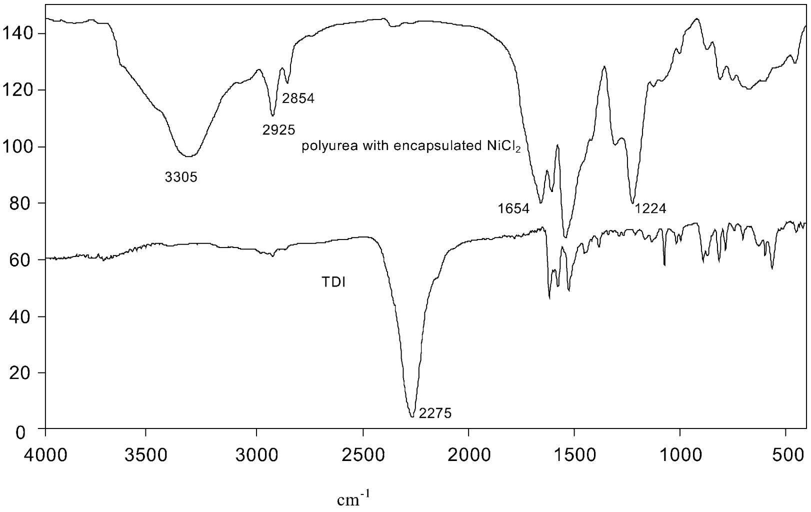


Fig. 1. FT-IR spectra of 2,4-TDI and polyureas with encapsulated $NiCl_2$.

analysis, accounting for the existence of polyurea. Atomic absorption spectrometry (AAS) gave the weight percentage of Ni ca. 2.62 (wt.%).

Scanning electron microscope and transmission electron microscope (TEM) were used to study the surface morphology and the nickel dispersion on the as-prepared microcapsule wall.

The surface morphology could be well illustrated according to Fig. 2, and the photographs reveals that the obtained microcapsules were sphere-like morphology, with the diameter ranging from 1 to 15 μm. However, very uniform structures including porosities and non-porous parts were well organized as shown in Fig. 3, and these diameters of either porosities or non-porous parts ranged from 20 to 40 nm, making these structures especially interesting for reaction and release control. These uniform porosities allow the vaporization of water inside the microcapsules during heating, thus the formation of hollow structure. The existence in the form of hollow microcapsule could be strongly evidenced from the surface morphology of broken microcapsules, and the thickness of microcapsule wall about 300 nm could be calculated from Fig. 4. Besides, the uniform of the interior surface could also be well observed; the enlarged photo about 50,000 folds could be found from Fig. 5, and similar surface morphology for interior surface could be obtained in comparison with the morphology for exterior surface.

From the above discussion, considering the interior and exterior surface of hollow microcapsules together with cross-section of microcapsule wall, that the size of porosities and non-porous parts were rather uniform ranging from 20 to 40 nm could be concluded.

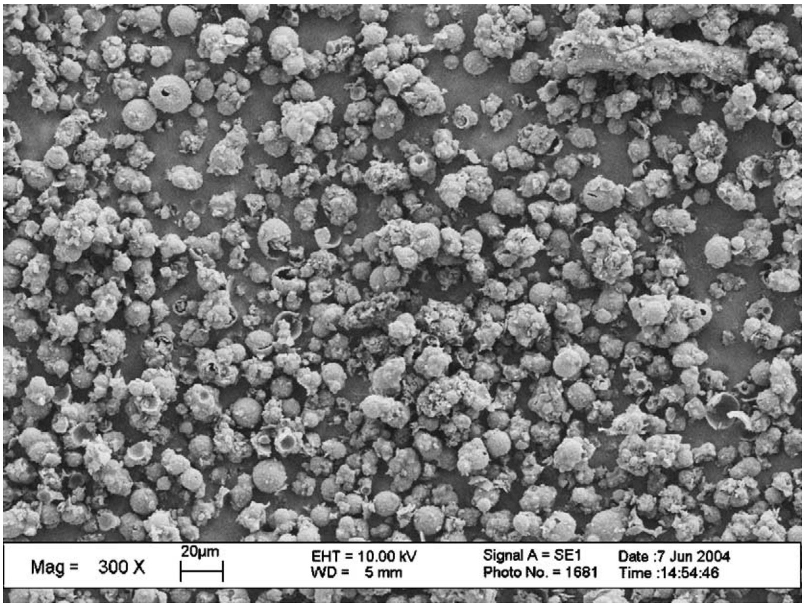


Fig. 2. The obtained polyurea microcapsule with encapsulated $NiCl_2$.

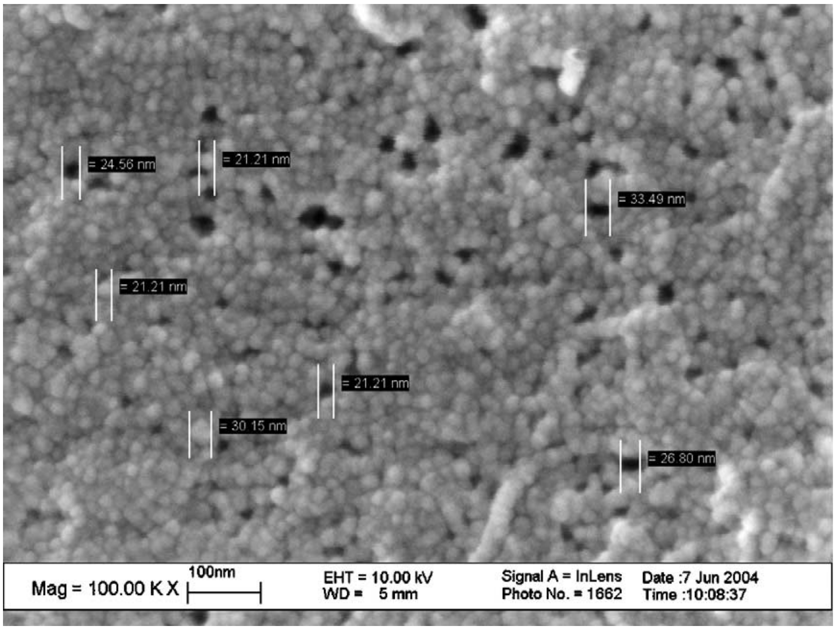


Fig. 3. Enlarged figure of exterior surface of microcapsule.

TEM image of as-prepared microcapsule gave that the dotted nickel particle could be found dispersed in the microcapsule wall, as shown in Fig. 6. This HRTEM image of the sample also revealed that the primary Ni nanoparticles had a diameter under 30 nm.

3.2. Thermal stability

Differential scanning calorimetry and thermogravimetry test indicated that the polyurea microcapsules were thermal stable and no decomposition could be observed under 200 °C. After no change for all the samples corresponding to the increase of temperature, endothermal peaks appeared at 250–350 °C, considered as the melting temperatures of the microcapsules; the corresponding spectra could be verified from TG test. No significant differences in both DSC and TG could be observed for the polyurea with and without $NiCl_2$, however, the existence of $NiCl_2$ in microcapsules improved the thermal stability; the corresponding peaks of the microcapsule with $NiCl_2$ in DSC and TG shifted toward higher temperature about 10 °C (Fig. 7).

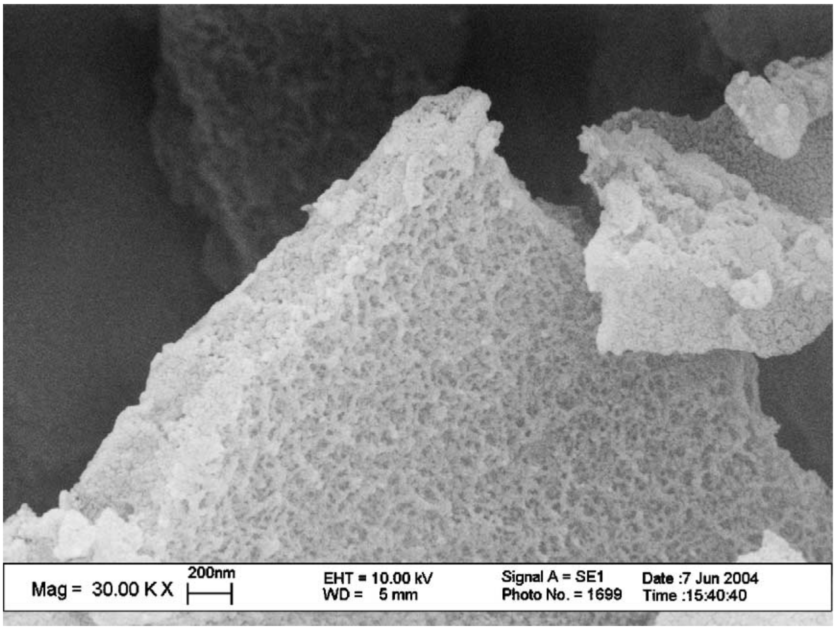


Fig. 4. Surface morphology of broken microcapsule.

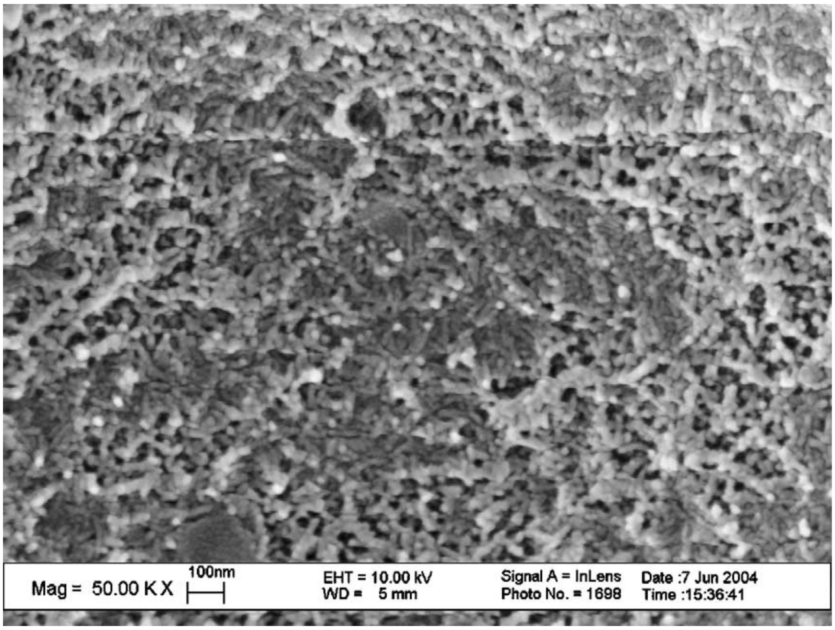


Fig. 5. The interior surface of microcapsule.

It could be also found that the unique residue after thermal process till 622 °C was $NiCl_2$ and the evidence could be observed from the following characterization from thermal analysis.

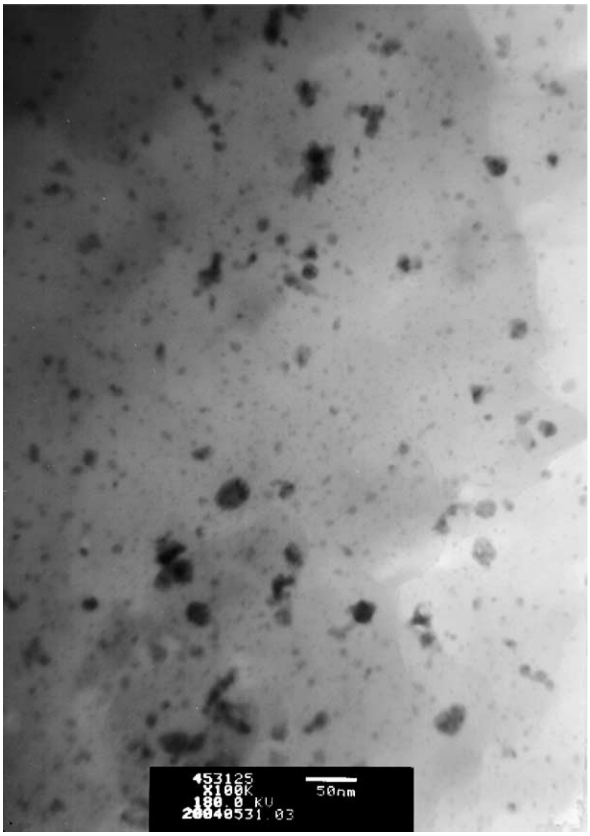


Fig. 6. TEM micrograph of a microcapsule.

When the temperature arrived at 500 °C, the weight loss reached 6.75 (wt.%), which is similar to the result 5.79 ($NiCl_2$ wt.%) obtained from AAS. When the temperature arrived at 622 °C, the weight loss reached 5.79% and kept constant despite the elevated temperature. It could be concluded that in the present research, TG provided a novel and reliable way to measure the content of encapsulated inorganic metals in polyurea microcapsules.

3.3. Chemical stability

Efficient entrapment of transition-metal based catalysts requires the design of systems possessing ligating functionality in order to retain the metal species. Polyurea microcapsules were found to be suitable by virtue of their chemical structure – a backbone of urea functionality – that could ligate and thus retain metal species. Here,

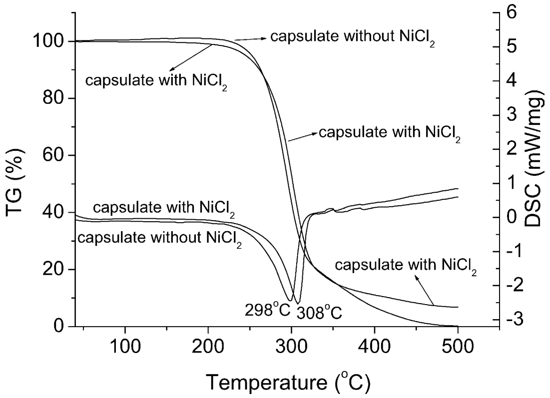


Fig. 7. DSC and TG results.

encapsulation efficiency of polyurea microcapsules produced by the interfacial polycondensation method was experimentally measured. When the solvents, such as ethanol, toluene and water were adopted to mix the microcapsules with $NiCl_2$, and heated even at 110 °C for 5 h, no nickel ion could be detected; the phenomena exhibit the chemical stability of encapsulated $NiCl_2$. This chemical stability will be further evidenced by recyclable reaction discussed later. Polyurea itself was capable of chelating with the metal species, eliminating the need to synthesize special chelating groups and incorporate them within the polymer matrix in separate steps [11].

The above findings are significant and imply that polyurea may function as a good support for an active species for reaction. This prompted an investigation to ascertain in reduction.

3.4. Benzaldehyde reduction

Reduction of benzaldehyde was adopted as a typical reaction to test the catalytic performance of microcapsule encapsulated with $NiCl_2$. The blank experiment for benzaldehyde reduction in the presence of $NaBH_4$ could be performed without catalyst, however the presence of nickel catalyst accelerated reduction and the catalytic reduction result is shown in Table 1.

The data presented in Table 1 show the effective promotion towards benzaldehyde reduction with heterogeneous microcapsules encapsulated with $NiCl_2$, as well as the corresponding data obtained using the homogeneous $NiCl_2$ catalyst. It could be well observed that the heterogeneous microcapsule catalyst proceeded smoothly. Furthermore, the used microcapsule catalyst could be collected simply by filtration and reused in benzaldehyde reduction, as shown in Table 2.

This heterogeneous microcapsule catalyst was reused fifth times with no loss of activity or selectivity. Analysis of the product mixtures gave no detection of nickel ion by the AAS method whose detection limit is 0.2 ppm.

Encouraged by the result from microencapsulation with $NiCl_2$, other inorganic metal salts, such as $CuCl_2$, $CoCl_2$, $Mn(NO_3)_2$ were used as core materials respectively for microencapsulation, similar results could be obtained, meaning the present microencapsulation is a universal method for encapsulating inorganic metal salts forming hollow microcapsule with metal salts dotted in the interior surface. This novel methodology provided a simple and convenient way to encapsulate and disperse inorganic metals salts, and might find versatile usage in immobilizing catalyst.

Table 1
Catalytic performance of benzaldehyde reduction with nickel catalysts

Entry	Catalyst	Conv. (%)	Yield (%)
1	/	58	58
2	Polyurea microcapsule with $NiCl_2$	>99	>99
3	$NiCl_2$	>99	>99

Reaction conditions: benzaldehyde (3 mmol), *i*PrOH (5 mL), catalyst (0.3 g, Ni: 0.13 mmol), $NiCl_2$ (0.1 g, Ni: 0.42 mmol), NaOH (2.5 mmol), $NaBH_4$ (7.9 mmol), 50 °C, 1 h.

Table 2
Reuse of microcapsules encapsulated with $NiCl_2$ for benzaldehyde reduction

Entry	Reuse time	Conv. (%)	Yield (%)
1	First	>99	>99
2	Second	>99	>99
3	Third	>99	>99
4	Fourth	>99	>99
5	Fifth	>99	>99

Reaction conditions: benzaldehyde (3 mmol), *i*PrOH (5 mL), catalyst (0.3 g, Ni: 0.13 mmol), $NiCl_2$ (0.1 g, Ni: 0.42 mmol), NaOH (2.5 mmol), $NaBH_4$ (7.9 mmol), 50 °C, 1 h.

The reported polyurea encapsulated with Pd or Os compounds was prepared via firstly forming O/W emulsion, followed by interfacial polymerization, dissolving the active species into organic phase is necessary to be encapsulated. Comparing the inorganic metal salts, which could be dissolved in water phase, with those metallorganics, which could be dissolved in organic phase, the present methodology provides a cost effective method to retain the metal species in the hollow microcapsules, which are physically robust and chemically inert to reaction conditions.

4. Conclusions

In conclusion, a facile, cost effective and novel fabrication method has been developed for encapsulating inorganic metal salts in polyurea, and forming hollow microcapsules, which is of thermally and chemically stable. The successful use of the encapsulated $NiCl_2$ microcapsule as a recyclable catalyst for benzaldehyde reduction proves an effective immobilization method.

Acknowledgements

We acknowledge the donors of the National Natural Science Foundation of China (no. 20306009 and 20225620) and the Guangdong Provincial Natural Science Foundation (31412).

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