One-pot synthesis of yolk-shell nanoreactors containing molybdenum oxide nanoparticles for epoxidation of olefins

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Abstract: We report a one-pot synthesis of MoO_x nanoparticles (NPs) encapsulated inside hollow silica spheres (MoO_x@HSS). The yolk-shell nanostructure is fabricated via a self-assembly approach using poly(acrylic acid) as an organic template and dodecyltrimethoxysilane (C_{12}TMS) as a pore-directing agent, which exhibits prominent reusability in the liquid-phase epoxidation of olefins with *tert*-butyl hydroperoxide (TBHP) owing to the presence of the protective silica shell.

Keywords: Yolk-shell nanostructure, Molybdenum oxide, Epoxidation of olefins

1. Introduction

Epoxidation of olefins to their corresponding epoxides is an important reaction for the production of epoxy resins, paints, and intermediates in many organic synthesis. From the environmental point of view, the development of an efficient and greener epoxidation process using reusable heterogeneous catalyst and safer oxidizing reagents is significantly important. Among a number of heterogeneous catalysts reported so far, molybdenum-based catalysts have shown promising activity; however, conventional catalysts often suffer from instability and poor catalyst reusability because of leaching of the active Mo species after successive catalytic cycles. A promising approach to overcome the above problem is encapsulation of MoO_3 nanoparticles (NPs) within hollow silica nanostructures. Hollow nanostructures encapsulating catalytic core components inside the permeable porous shell (so-called yolk-shell nanostructures) have recently emerged as promising candidates for nanoreactors that efficiently catalyse the chemical reactions of specific reactant molecules[1-2]. The surrounding porous shell prevents the leaching of the catalysts under harsh reaction conditions or during the recycling process, while allowing the access of small reactant molecules to the cores, and thus allows the chemical reactions to efficiently occur within the protective void space.

To inhibit the leaching of Mo species, we in this study designed MoO_x NPs encapsulated inside porous hollow silica spheres (MoO_x@HSS) via a simple one-pot method. The fabrication of MoO_x@HSS was performed by a self-assembly approach using poly(acrylic acid) (PAA) as an organic template[3]. An organo-silane coupling agent (dodecyltrimethoxysilane; C_{12}TMS) was added as a pore-directing agent together with a typical alkoxysilane (tetraethoxy orthosilicate; TEOS), followed by calcination in air, to form permeable porous silica shells. The synthesized catalyst exhibited prominent reusability with a modest catalytic activity in the liquid-phase epoxidation of olefins owing to the presence of the protective silica shell, making it an effective heterogeneous catalyst for the selective transformation of olefins into their corresponding epoxides.

2. Experimental

The MoO_x@HSS were fabricated by a PAA-templated self-assembly approach[3]. In a typical synthesis, an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot H_2O$, PAA and aqueous ammonia were mixed to obtain transparent solution. Ethanol and $NaBH_4$ aqueous solution were subsequently added to obtain colloidal solution containing MoO_x NPs-PAA aggregates. Into this solution were added TEOS and C_{12}TMS to achieve silica/organo-silica network formation. The resulting precipitate was recovered and calcined at 500 °C to yield MoO_x@HSS.

3. Results and discussion

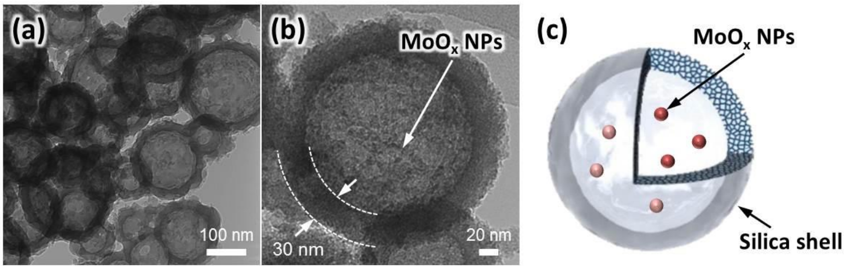

Figure 1. (a, b) TEM images of MoO$_x$@HSS, (c) Illustration of the structure of MoO$_x$@HSS

The TEM images showed that MoO$_x$@HSS possesses hollow cavities surrounded by silica shells of ca. 30 nm thickness and nano-size MoO$_x$ particles were observed within the internal cavities. The average diameter of MoO$_x$ NPs was estimated to be 5.8 nm (Figure 1). The N_2 physisorption isotherm of MoO$_x$@HSS without C$_{12}$TMS showed a typical type-III isotherm, indicative of a non-porous solid. On the other hand, MoO$_x$@HSS synthesized with an optimum amount of C$_{12}$TMS showed a clear hysteresis loop closing at p/p_0 = 0.5, which is typical for hollow nanostructured material. Comparison of BJH pore distribution curves indicated that MoO$_x$@HSS with C$_{12}$TMS has an extended porosity in the meso-pore region with an average pore diameter of 2.1 nm. These results demonstrate that MoO$_x$@HSS has hollow cavities and the addition of C$_{12}$TMS enhances the meso-porosity in the silica shell.

The catalytic performance of the thus synthesized MoO$_x$@HSS catalyst was examined in the liquid-phase epoxidation of cyclooctene using *tert*-butyl hydroperoxide (TBHP) as an oxidant. MoO$_x$@HSS showed a higher activity (80% conversion at 8 h) than MoO$_x$@HSS synthesized without C$_{12}$TMS (27% conversion at 8 h) (Figure 2 (a)), demonstrating that increased porosity in the silica shell improves the mass transfer and accessibility of reactant molecules to the MoO$_x$ NPs core. Moreover, MoO$_x$@HSS was reusable over five repeated cycles without a major loss of activity, whereas the conventional MoO$_x$/SiO$_2$ catalyst showed a continuous activity reduction during the reusability test due to the transformation/leaching of Mo species (Figure 2 (b)). This result demonstrates that MoO$_x$@HSS acts as a reusable heterogeneous catalyst owing to the ability of the protective silica shell to inhibit the leaching of Mo species.

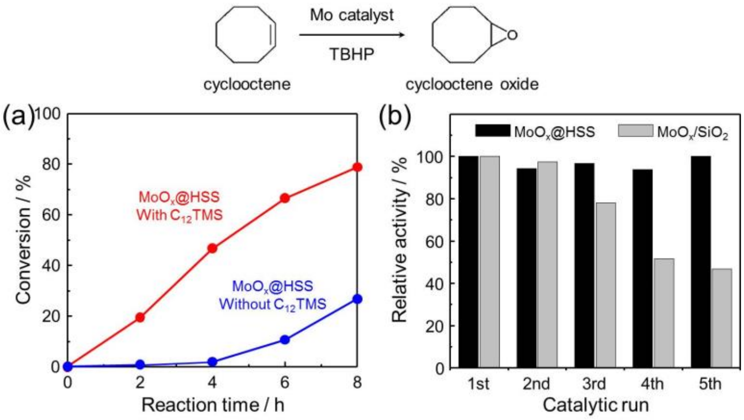

Figure 2. (a) Reaction kinetics in the epoxidation of cyclooctene over MoO$_x$@HSS and MoO$_x$@HSS synthesized without C$_{12}$TMS, (b) Reusability test over MoO$_x$@HSS and MoO$_x$/SiO$_2$. Reaction conditions: catalyst (75 mg), cyclooctene (1 mmol), TBHP (1.2 mmol), 1,2-dichloroethane (5 mL), and 80 ºC.

4. Conclusions

A yolk-shell nanostructured catalyst consisting of tiny MoO$_x$ NPs (MoO$_x$@HSS) was fabricated through a facile one-pot method utilizing poly(acrylic acid) as a sole organic template. Encapsulation of MoO$_x$ NPs inside the hollow silica spheres could afford a heterogeneous catalyst active for olefin epoxidation, which was reusable over at five cycles without any significant loss of catalytic performances owing to the ability of the silica shell to inhibit the leaching of Mo species. We expect that this yolk-shell nanocomposite catalyst can find diverse applications in industrially important catalytic oxidation reactions.

References

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