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Novel sea urchin-like polyaniline microspheres-supported molybdenum catalyst: Preparation, characteristic and functionality

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ABSTRACT

Novel heterogeneous molybdenum catalysts were successfully synthesized using sea urchin-like polyaniline (PANI) hollow microspheres constructed with their own oriented nanofibers arrays as support. This catalyst was successfully applied for efficient epoxidation of olefins using tert-butylhydroperoxide (TBHP) as oxidant. The catalytic activity of the PANI microspheres-supported catalysts (95% conversion) was found to be higher than that observed for its corresponding homogenous catalyst (85% conversion) and the conventional PANI-supported catalyst (65% conversion). The immobilized catalyst showed a stable catalytic activity in manifold reuses. It was found that the special micro/nanoscale spherical morphology plays an important role for the enhancement of activities of the polymer-supported heterogeneous catalyst.

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1. Introduction

Olefin epoxidation is an important reaction because epoxides are widely used in the production of epoxy resins, paints, perfumes and surfactants and are also intermediates in many organic syntheses [1–3]. In order to make the epoxidation process cleaner, safer and more efficient, the use of catalysts is mandatory. Over the last few decades, the application of soluble compounds of early transition metals such as Mo, W, Ti and V, as homogeneous catalysts for olefin epoxidation, has been reported [4]. Among the molybdenum complexes, peroxo molybdenum (VI) complexes have been demonstrated to be efficient, clean and environmental benign catalysts in the petrochemical process of olefins epoxidation by alkyl hydroperoxides [5–7]. Good activities and selectivities have been pointed out as the main advantages of homogeneous catalysts. However, some industrial problems such as corrosion, deposition on reactor wall and difficulty in recovery and separation of the catalyst from reaction products are associated with these homogeneous catalysts. The immobilization of homogeneous catalysts has therefore attracted a lot of attention. Because of easy separation of the product from the reaction medium, along with the recovery and reuse of these expensive catalysts, the heterogenized catalysts provide an attractive advantageous over homogeneous catalysts [8,9]. Recently, anchoring of catalytically active transition metal complexes onto a polymer matrix has received considerable attention [10] due to their potential advantages in practical synthesis, i.e., (i) the catalyst is easily separated from the reaction solution by filtration or centrifugation, (ii) the recovered catalyst can be used repeatedly. For instance, Grivani et al. [11–13] have used polymer-bound piperazine or polystyrene as a robust support for immobilization of $Mo(CO)_6$ to epoxidize various alkenes. Sherrington's group [14–17] has synthesized polystyrene, polymethacrylate, polybenzimidazole and polysiloxane resins for immobilization of Mo(VI) catalysts derived from $MoO_2(acac)_2$ and has investigated their catalytic activity in the alkene epoxidation with *t*-butyl hydroperoxide (TBHP). However, the complex synthesis procedures for the polymer supports and the lowered activity of the heterogeneous catalyst than that of their corresponding homogenous ones limit the use of even the heterogeneous catalysts for the epoxidation process. This situation necessitates the development of a novel polymer-supported heterogeneous catalyst that can combine the advantages of both, homogenous and heterogeneous catalysis in order to obtain an efficient catalyst.

In order to accomplish the need, we have chosen polyaniline (PANI) as a support material because of its distinctive characteristics such as facile preparative protocols from cheap starting material (aniline), high environmental stability and non-solubility in most of the organic solvents. PANI is of strong interest because of its large conductivity range, good thermal stability and, especially in doped state, high resistance against common solvents; in this respect, it should be an appropriate support material for catalytic processes in gas and liquid phases. Furthermore, the amino group in the main chain of PANI can offer a great opportunity to covalently bind transition-metal, which make it a promising candi-

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date for using as supports in the heterogeneous catalysis. The most interesting property of PANI is that, depending on the oxidation state of the aniline polymers, several different forms may arise. The transition to the metallic state takes place without any change in the number of electrons; the quinonoid units of the emeraldine salt are converted to benzenoid units by a proton-induced spin-unpairing mechanism that leads to two unpaired electrons. Recently, PANI-supported metal catalysts, such as molybdenum [18–22], vanadium [23], indium [24], palladium [25,26], cobalt [27], palladium salts [28], and rhenium oxides [29] have been synthesized and applied in modern organic synthesis. Since the discovery of carbon nanotubes in 1991 [30], nanostructured PANI has become an intensive research subject and various morphologies such as nanotubes [31–33], nanobelts [34], nanofibers [35–38] and hollow microspheres [39] have been synthesized using various strategies. It is well-known that nano-scaled materials have a distinctive size effect that leads to unique chemical and physical properties different from than those of bulk materials. Therefore, it is appropriate to expect that the heterogeneous catalyst with nano-structured polymer as supports will result in different catalytic properties. Apart from that, immobilization of metal catalyst using nano-structured PANI as support has seldom been reported yet.

The above discussion offers us to use nano-structured PANI instead of conventional PANI to immobilize Mo catalyst in the epoxidation of olefins. This improvement permits to turn to the advantages of both homogeneous (enantioselectivity, activity) and heterogeneous (separation, recovery, recycling) catalysts. Therefore, the immobilization of homogeneous catalysts allows us to overcome the problems with separation and reuse and, thus, greatly amends the properties of the catalysts and their commercial value.

We herein report the successful synthesis of the novel heterogeneous Mo catalysts with sea urchin-like PANI hollow microspheres as support. The structure of the PANI microspheres-supported catalysts has been identified with the help of TEM, FTIR, EDX and XPS spectrum. The GC-MS measurements have shown that PANI microspheres-supported catalyst has enhanced catalytic activity (95%, conversion) for the epoxidation of olefins using TBHP as oxidant than that of the conventional PANI-supported catalyst (65%, conversion). The mechanism of olefin epoxidation with PANI microspheres-Mo catalyst is also discussed.

2. Experimental

2.1. General

Aniline, $FeCl_3{\cdot}6H_2O$ and HCl were purchased from Beijing Chemical Reagent Company. Polymer hollow spheres were obtained from Rohm & Haas. Commercial PANI were obtained from Chang Chun Reagent Company. Aniline was freshly distilled under reduced pressure before use. Other reagents were used as received without further purification.

2.2. Synthesis of the PANI hollow spheres and homogenous molybdenum catalyst

In a typical procedure [40], 0.02 mol of aniline was added to 30 ml of HCl (1 M) aqueous solution under stirring to yield a uniform solution. 53 mg of the hollow PS spheres dispersion (solid content 37 wt%) was added into the above solution and the mixture was kept under magnetic stirring for 24 h to allow an equilibrium uptake. The hollow spheres preloaded with anilinium salt were centrifuged and washed with de-ionized water, followed by dispersing into 100 ml of $FeCl_3$ (0.1 M) aqueous solution at room temperature to initiate the oxidative polymerization. When the colour of the mixture had become green, the mixture was further left to react for another 15 h. The resulting PANI precipitate was washed several times with de-ionized water, methanol and ether respectively. Finally, the PS templates were removed with tetrahydrofuran (THF) to obtain pure sea urchin-like PANI hollow microspheres.

Homogenous $MoO(O_2)_2(DMF)_2$ complexes were synthesized according to the procedure illustrated in the literature [41]. MoO_3 (1 g, 6.95 mmol) was dissolved in excess of H_2O_2 (5 ml, 30%) and the system was subjected to stirring for 4 h at 40 °C. Then the solution was cooled overweight and subsequently N,N-dimethylformamide (DMF) (5.6 ml, 0.014 mol) was added. After stirring for 2 h, the solution was vaporized at 40 °C until the appearance of the yellow solid. Following the yellow solid appearance, the system was cooled at 5 °C for one week. The obtained yellow crystals were filtered out and had been washed with ether.

2.3. Synthesis of PANI microspheres-supported molybdenum catalyst

The heterogeneous PANI hollow microspheres-supported Mo catalyst was prepared by stirring a mixture of the sea urchin-like PANI hollow microspheres (300 mg) and homogenous $MoO(O_2)_2(DMF)_2$ (300 mg) in acetonitrile (15 ml) at room temperature for 48 h. Afterwards, the solid was filtered out and dried under vacuum after washing with acetonitrile to give black powder. Catalysts with the commercially PANI as support were also synthesized under the same experimental conditions for a comparative study purpose.

2.4. Catalytic epoxidation of olefins by TBHP

The epoxidation of cis-cyclooctene was carried out using TBHP as an oxidizing agent. The experimental procedure is as follows: cyclooctene (1.84 ml) and the PANI hollow microspheres supported Mo catalyst (0.12 g) were stirred at ca. 60 °C in $CHCl_3$ (8 ml) using TBHP (4.8 ml) as an oxidizing agent for 12 h. After filtering off the catalyst, the filtrate was analyzed by GC-MS using an internal standard technique.

2.5. Reusability of the catalyst

The reusability of the sea urchin-like PANI hollow microspheres-supported molybdenum was studied in repeated epoxidation reaction of cyclooctene. The reactions were carried out as described in above section. At the end of each reaction, the catalyst was filtered out, washed with 4×8 ml $CHCl_3$, dried in an oven at ca. 60 °C and then reused.

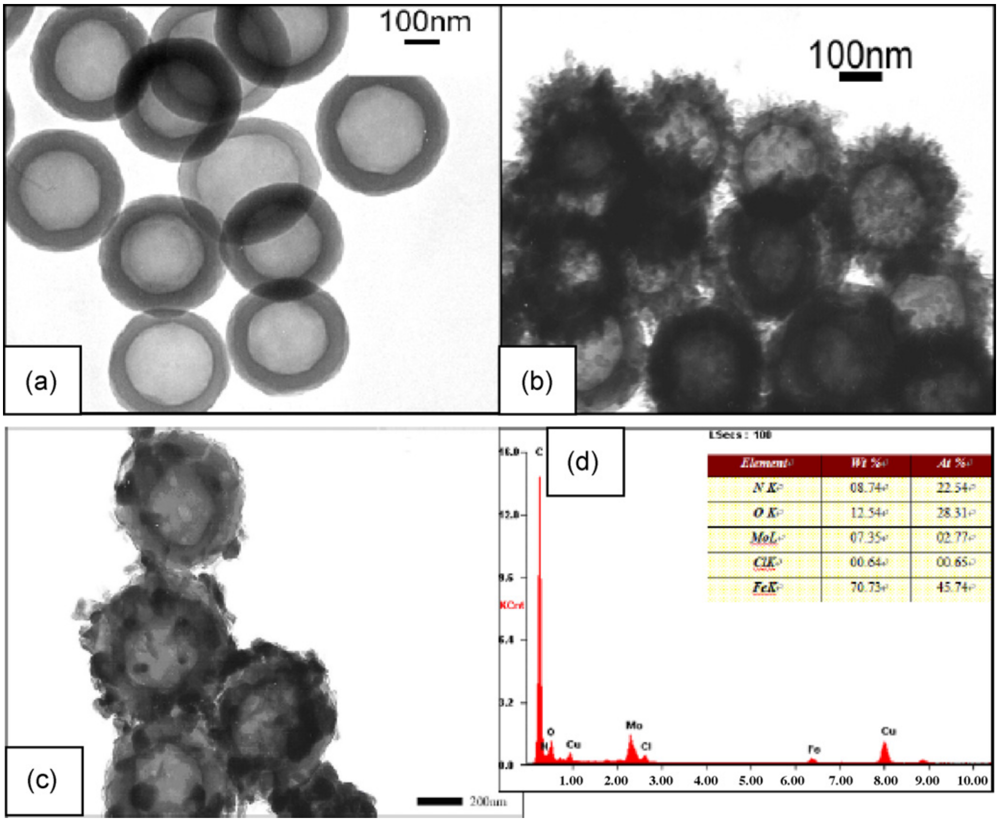
2.6. Characterization

A JEOL 100CX transmission electron microscope with EDX operating at an acceleration voltage of 100 kV and a JEOL 6700F field-emission scanning electron microscope operating at a voltage of 3 kV were used to characterize the morphologies of the product. FTIR spectra were recorded on an infrared spectrophotometer (NEXUS670) using KBr pellets samples. GC-MS analysis was performed on an HP-6890 series equipment with an FID detector.

3. Results and discussion

3.1. Synthesis of the heterogeneous PANI hollow microspheres-supported molybdenum catalyst

According to our previous published work [40], the sea urchin-like PANI hollow microspheres are synthesized by a self-assembly process using commercial polystyrene (PS) hollow spheres template. The transmission electron microscopy (TEM) images of PS



Element	Wt %	At %
N K	08.74	22.54
O K	12.54	28.31
MoL	07.35	02.77
ClK	00.64	00.65
FeK	70.73	45.74

Fig. 1. The typical transmission electron microscopy (TEM) images of (a) pure PS spheres template; (b) the resulting sea urchin-like PANI hollow spheres; (c) the sea urchin-like PANI hollow microspheres-supported Mo catalyst; (d) EDX spectrum of the sea urchin-like PANI microspheres-supported Mo catalyst.

hollow spheres and the resulting PANI complex hollow spheres are shown in Fig. 1a and b. It can be found that the template spheres have hollow structure with an average diameter of 400 nm. It is clear that the resulting PANI has the same hollow spherical structure as that of the PS template and the shell of the PANI microspheres consists of radially aligned nanofibers with 15–20 nm in average diameter and 50–180 nm in average length, resulting in the formation of novel sea urchin-like morphology.

$MoO(O_2)_2(DMF)_2$ is prepared using a method that has been previously discussed in the literature [41]. As mentioned earlier in the experimental part, the PANI hollow microspheres-supported Mo catalyst is prepared by stirring a 1:1 mixture of the sea urchin-like PANI hollow microspheres and $MoO(O_2)_2(DMF)_2$ in acetonitrile for 48 h at ambient temperature. Results of catalyst characterization by TEM have been shown in Fig. 1c. It is revealed that after immobilization reaction, the morphology of the PANI-Mo catalyst has become slightly different from that of the sea urchin-like microspheres support. It is observed that nanofibers on the surface of the hollow microspheres have become thicker. Also some irregular solid dark spots attached to the fibers are detected, which have been verified by EDX analysis to be Mo with 7.35 wt% as shown in Fig. 1d. The presence of these solid dark spots provides the fact that the Mo catalyst is successfully immobilized on the surface of PANI microspheres.

Evidence of the sample's nature and the immobilization of the Mo catalyst on the PANI microspheres is further provided by FT-IR spectra shown in Fig. 2. The sea urchin-like hollow microsphere is identical to the emeraldine salt form of PANI. All characteristic bands of PANI, including the C=C stretching deformation of quinoid at 1580 cm^{-1}, benzenoid rings at 1496 cm^{-1}, the C—N stretching of secondary aromatic amine at 1302 cm^{-1}, the aromatic C—H in plane bending at 1141 cm^{-1} the out-of-plane deformation of C—H in the 1,4-disubstituted benzene ring at 821 cm^{-1} and 505 cm^{-1} are observed [42–44]. Characteristic IR bands of homogenous $MoO(O_2)_2(DMF)_2$ appears at 1697 cm^{-1} (C=O band of DMF), 964 cm^{-1} (Mo=O band), 868 cm^{-1} and 789 cm^{-1} (Mo-O-Mo bands) respectively [45]. It is noteworthy that the peak at 1697 cm^{-1} of C=O band attributable to DMF in $MoO(O_2)_2(DMF)_2$ has omitted. Other characteristic IR bands of $MoO(O_2)_2(DMF)_2$ (Mo=O and Mo-O-Mo bands) and PANI have been observed in the spectrum of the PANI microspheres-supported Mo catalyst appear at slightly shifted positions as compared to those in the spectrum of the unsupported Mo

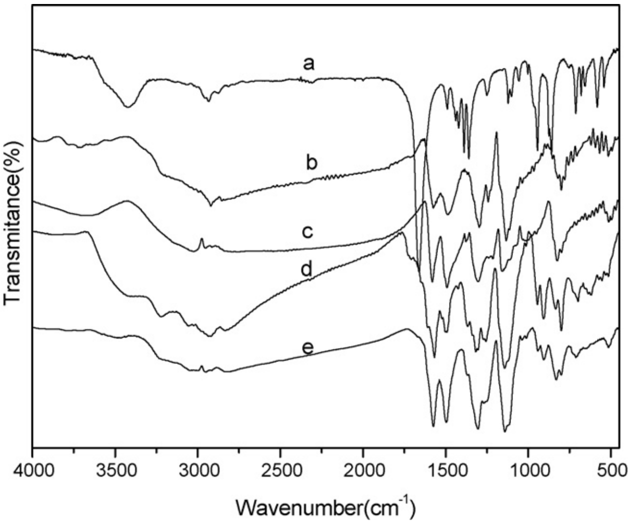


Fig. 2. FTIR spectra of (a) homogenous $MoO(O_2)_2(DMF)_2$ catalyst; (b) pure sea urchin-like PANI hollow microspheres; (c) commerical PANI powder; (d) heterogeneous sea urchin-like PANI microspheres-supported Mo catalyst; (e) heterogeneous commerical PANI-supported Mo catalyst.

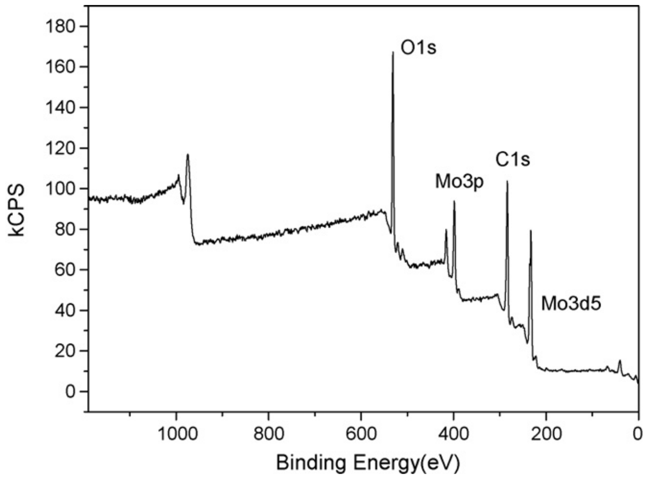


Fig. 3. XPS spectrum of heterogeneous sea unrchin-like PANI microspheres-Mo catalyst.

and PANI, indicating a strong interaction between the Mo catalyst and the PANI support.

A key to a better understanding offer X-ray Photoelectron Spectroscopy (XPS) investigations of the PANI-Mo catalysts, as they are sensitive to the surface and not only provide information about the electronic state of Mo, but also about the nitrogen atoms in the PANI chains. XPS wide scan of the samples is shown in Fig. 3. After comparison of the spectrums of pure PANI and PANI hollow microspheres-supported Mo catalyst, it has been discovered that the spectrum of the PANI hollow microspheres-supported Mo catalyst contains two new additional peaks at 233.25 eV and 398.3 eV apart from all the peaks those have been observed in the spectrum of the pure PANI. The peak positions correspond to Mo_{3d} and Mo_{3p}, further testify the presence of Mo on the surface of the heterogeneous catalyst.

3.2. Catalytic epoxidation of olefins using THBP as oxidant

The catalytic activity of the resulting sea urchin-like PANI hollow microspheres-supported Mo catalyst catalyst has been initially investigated in the epoxidation of cyclooctene in the presence of tert-butylhydroperoxide (THBP). The reaction has been carried out in $CHCl_3$ in which higher epoxide yield is observed. The comparison of catalytic activity of the same amount of $MoO(O_2)_2(DMF)_2$ as homogenous catalyst and commercial bulk-PANI as support has also been carried out.

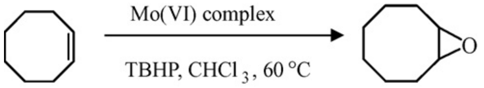
The activity and selectivity of sea urchin-like PANI microspheres-Mo, homogenous $MoO(O_2)_2(DMF)_2$ and commercial bulk PANI-supported Mo for epoxidation of cyclooctene are determined by GC-MS (Table 1). Clearly, transition-metal Mo(VI) complexes is a very effective catalyst for epoxidation of alkenes with a high epoxidation conversion of 85% and these results are in good agreement with previous reports [5–7]. Transition-metal complexes are very effective catalysts for a variety of organic reactions but one of the major problems, which were associated with these homogeneous catalysts, is the recovery of catalyst from the reaction medium. The use of polymer-supported catalysts in organic transformation ions has been receiving extraordinary attention and the design of functionalized polymers carrying catalytically active metal species has generated considerable interest. However, the conversion with these polymer-supported catalysts is found to be generally lower than that of their corresponding homogenous catalysts [46]. It is very interesting to observe from Table 1 that the conversion of cyclooctene by using the sea urchin-like PANI hollow microspheres-Mo is very high (95%), which is even higher than that has been obtained with homogenous Mo catalyst (85%). On the other hand, the catalytic performance of commercial bulk-PANI as support is poor and provides a low conversion of only 66%. Hence, it is evident that the catalytic performance of the sea urchin-like PANI hollow microspheres-Mo catalyst is superior to that of the classical bulk PANI-Mo catalyst. The possible reason is provided in the mechanism section illustrated below.

In order to verify the catalytic scope of the sea urchin-like PANI microspheres-Mo catalyst, it has also been applied for epoxidation of a wide range of alkenes (Table 2). It is found that this catalyst efficiently converts both cyclic and linear alkenes to their corresponding epoxides. From first to third entries in Table 2, it can be found that carbocyclic alkenes are efficiently converted to the corresponding epoxides in high conversion. However, oxidation of the aromatic and linear alkenes requires longer reaction times than that of the carbocyclic alkenes (entries 4th and 5th).

The reusability of a supported catalyst is one of the most important benefits of these catalysts, because transition-metal complexes are often expensive to purchase or prepare [47]. Therefore, the reusability of the PANI microspheres-Mo catalyst has also been monitored. After the first and all following catalytic runs of the PANI microspheres-Mo catalyst, the recovering procedure of the catalyst is the following: the PANI microspheres-Mo catalyst is separated by simple filtration, washed with acetone, dried in an oven and then reused. The persistence of the catalytic activity has been checked for six consecutive runs in the epoxidation of cyclooctene. The results are summarized in Table 3, where it is seen that in the first two runs the immobilized catalyst has exhibited a higher activity in epoxide formation in comparison to the following runs. After two runs the catalytic activity remains constant without a significant loss. These results indicate that most of the Mo complexes are highly dispersed and anchored tightly to the nitrogen atom at the surface of the PANI hollow microspheres via chemical immobilization. Thus the PANI microspheres-Mo catalyst maintains its catalytic activity with no leaching of the metal complex in residual repeated uses, except a small amount of Mo complex that has been absorbed physically on the PANI matrix and can be wiped off the mixture after first run.

In order to further verify whether the observed catalysis is truly heterogeneous or not, the following experiment has been addi-

Table 1
Epoxidation of cyclooctene to the corresponding epoxides with TBHP catalyzed by PANI microspheres-supported Mo, conventional PANI-supported Mo and homogenous Mo catalysts under reflux condition.[a]

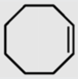
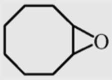
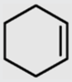
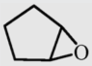
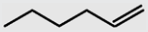
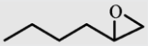
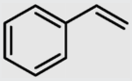
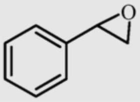


Catalyst	Time (h)	Conversion (%)	Selectivity (%)	BET surface area (m^2/g)
PANI microsphere-Mo	6	95	97	62
Commerical PANI-Mo	6	66	99	39
Homogeneous Mo	6	82	97	–

[a] Reaction conditions: cyclooctene (1.84 ml), TBHP (4.8 ml), PANI hollow microspheres-Mo catalyst (0.12 g), commerical PANI-Mo catalyst (0.12 g), equative homogeneous Mo catalyst (0.06 g), $CHCl_3$ (8 ml); reaction temperature: 60 °C.

Table 2
Epoxidation of selected olefins catalyzed by sea urchin-like PANI hollow microspheres-supported Mo catalyst with TBHP under reflux condition.[a]

$$\text{Olefin} \xrightarrow[\text{TBHP, CHCl}_3\text{, 60 °C}]{\text{PANI microspheres} - \text{Mo(VI)}} \text{Epoxide}.$$

Entry	Substrate	Time (h)	Product	Conversion (%)	Selectivity (%)
1		6		95	97
2		6		83	97
3		6		81	98
4		12		78	97
5		12		73	97

[a] Reaction conditions: cyclooctene (1.84 ml), TBHP (4.8 ml), PANI hollow microspheres-supported Mo catalyst (0.12 g), $CHCl_3$ (8 ml); reaction temperature: 60 °C.

tionally performed. The epoxidation of cyclooctene with the PANI microspheres-Mo catalyst under the same conditions as described above is again used as the model. As shown in Table 1, with the reaction completion time of 6 h, the conversion of cyclooctene is around 95%. While, when the reaction has been carried out for 2 h, the conversion is only 4% as determined by GC, indicating that catalytic reaction is just at the beginning stage. Simultaneously, the solid is removed from the reaction mixture by filtration and the reaction is allowed to be continued with remaining filtrate under same conditions. Afterwards, with the completion time of 6 h, the conversion is found to be only <10%. This result testifies the fact that olefin epoxidation cannot continue without the solid catalyst in the residue and hence confirming that the new synthesized catalyst is truly heterogeneous.

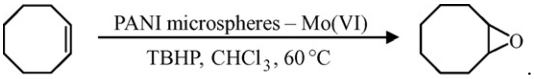
3.3. Mechanistic aspects of olefin epoxidation with PANI microspheres-Mo catalyst

As described that the PANI hollow microspheres-Mo catalyst is synthesized by blending the sea urchin-like PANI hollow microspheres with $MoO(O_2)_2(DMF)_2$ in acetonitrile. As it is shown in Scheme 1a that PANI contains the amino group with N donor atoms in its main chain, which provides the possibility for transition-metal Mo and its tentative structure to be covalently bound.

Generally, the Mo(VI) diperoxo complex is considered as the catalytically active center for epoxidation of alkenes by homogeneous as well as heterogeneous routes [48]. The molecular oxygen-transfer mechanism in epoxidation of olefin with Mo(VI) has been extensively investigated by many research groups and two main hypotheses have been accepted to be dominated. Mimoun [49,50] has suggested a stepwise pathway in which the olefin coordinates to the metal atom before subsequent insertion into a Mo-O (peroxo) bond to form a five-membered metallacycle. On the other hand, Sharpless [51] has proposed a concerted reaction mechanism involving a direct attack by the olefin on the peroxo oxygen atom with a three-membered ring inrermediate (including the two carbon atoms of the olefin and the transferred oxygen). The two seminal studies are contradictory and have caused a long-lasting debate [52]. Until recently, with the help of modern quantum chemistry [53,54], the mechanism has been finally clarified and the three-membered transition state (essentially consistent with the Sharpless mechanism) has been accepted. According to the Sharpless mechanism, the possible epoxidation process is catalyzed by PANI-Mo(VI) and has been illustrated in Scheme 1b.

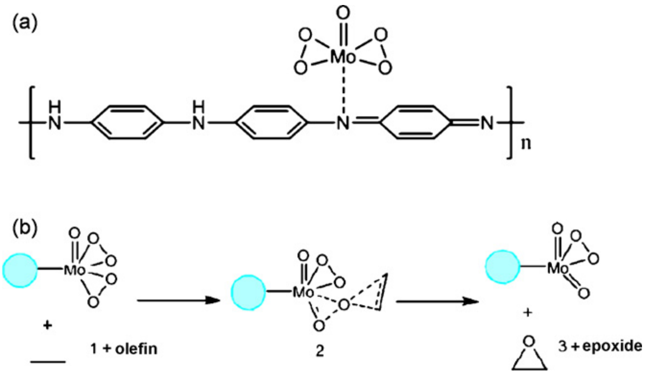
Generally, the efficiency of heterogeneous immobilized catalysts is found to be lower than that of their corresponding homogenous ones. Use of the commercial bulk-PANI as support in this study gives only 66% conversion, which is much lower than the conversion value (85%) for homogenous Mo(VI) complexes. However, the sea urchin-like PANI hollow microspheres-Mo catalyst results in a superior performance (95%, conversion) over not only the com-

Table 3
Recycling of sea urchin-like PANI hollow microsoheres-supported Mo catalyst in epoxidation of cyclooctene with TBHP under reflux condition.[a]



Run	Conversion (%)	Selectivity (%)	Time (h)
1	95	97	6
2	92	96	6
3	85	97	6
4	85	98	6
5	85	98	6
6	85	98	6

[a] Reaction conditions: cyclooctene (1.84 ml), TBHP (4.8 ml), PANI hollow microspheres-supported Mo catalyst (0.12 g), $CHCl_3$ (8 ml); reaction temperature: 60 °C.



Scheme 1. (a) Proposed polyaniline-supported Mo(VI) diperoxo complex structure. (b) Olefin epoxidation mechanism with PANI-Mo(VI) diperoxo complex suggested by Sharpless [45].

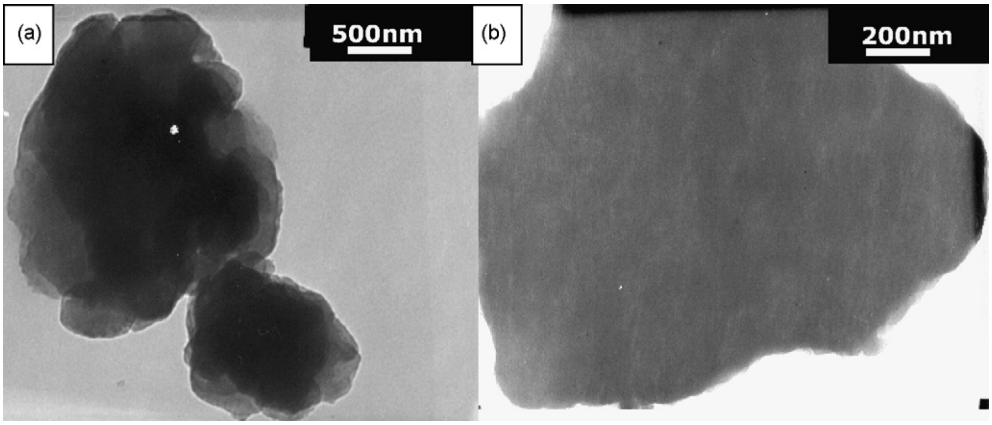


Fig. 4. The TEM images of commerical PANI powder: (a) low magnification; (b) high magnification.

mercial support but also the homogenous ones. The IR adsorption spectrum of the commercial PANI-Mo and PANI microspheres-Mo indicates that the structures of two catalysts are identical (as shown in Fig. 2). However, it can been seen from Fig. 4 that the morphology of the commercial PANI is a ruleless agglomerate, which is very different from the spherical morphology of the sea urchin-like PANI, suggesting that special micro/nano-morphology of support is beneficial in enhancing the catalytic performance of heterogeneous catalysts. BET measurements show that PANI microspheres have larger surface area than that of the commercial PANI (Table 1), which results in the possibility for higher Mo content. This phenomenon can be attributed to the fact that the surface area of the support is proportional to the metal content in a general fashion. It is well-known fact that [55], in order to achieve higher conversion by using polymer-bound catalysts, it is necessary for the active centers site on the surface and in the bulk of the particles to be accessible for the reactant molecules. Therefore, the enhanced catalytic performance of the PANI microspheres-Mo catalyst may be attributed to the finely and molecularly dispersed Mo (VI) species on the enlarged surface of the support, have been attached via chemical immobilization.

4. Conclusions

In summary, a novel, robust, highly effective and recyclable sea urchin-like PANI hollow microspheres-Mo catalyst has been successfully synthesized, characterized and applied for epoxidation of cyclooctene using TBHP as oxidant. This supported heterogeneous catalyst is found to be highly reactive in the epoxidation of a wide range of alkenes such as linear and cyclic alkenes. The PANI microsphere-Mo catalyst has shown the higher activity than that of its homogenous analogue. Also, the catalyst has the advantages of ease of separation from the product mixture, recovery and recycling in the reaction system. It has been revealed that the PANI microsphere-Mo catalyzed epoxidation of olefin follows the sharpless mechanism for the molecular oxygen-transfer in epoxidation of olefin with Mo (VI). It is found that the special micro/nanoscale spherical morphology plays an important role for the enhancement of catalytic properties of the polymer-supported heterogeneous catalyst. Therefore, high catalytic performance of the sea urchin-like PANI microspheres-Mo catalyst and easiness of catalyst recovery in the liquid-phase reaction make it a suitable candidate for an energy-saving epoxidation process of olefins. Precisely in this regard, we expect that sea urchin-like PANI microspheres as support material offers novel alternatives for the rational design of catalysts with desired features.

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