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ARTICLE TYPE

Novel chitosan-based/montmorillonite/palladium hybrid microspheres as heterogeneous catalyst for Sonogashira reactions

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The objective of this study was to develop novel chitosan-based/montmorillonite/palladium (CS /MMT/Pd) hybrid microspheres catalysts with improved properties for use in Sonogashira reactions. Interactions between chitosan matrix and montmorillonite nanofiller were revealed by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric (TG) analysis. The results confirmed the formation of intercalation structure between CS macromolecules and MMT layers. X-ray photoelectron spectroscopic (XPS) and high resolution transmission electron microscope (HR-TEM) analysis results showed that the Pd species with different valence dispersed in nano-level both in the CS matrix and the interlayers of MMT. CS/MMT/Pd hybrid microspheres were highly active for the Sonogashira reactions of aryl iodides and alkynes at a palladium catalyst loading of 0.3 mol %. And it can be recycled for 10 times without significant decrease in coupling yields. It was concluded that introducing MMT into CS matrix will effectively improve the thermal stability and Pd leaching-resistance of the hybrid microsphere catalysts. The results in this study demonstrated that the great potential of such heterogeneous catalysts applied in Sonogashira reactions.

Introduction

In organic synthesis, palladium-catalyzed C-C and C-X coupling reactions are among the most useful methodologies.[1] It is usually employed in the homogeneous system but causing difficulties in separation, recovery and reuse of palladium metal.[2] To avoid or at least mitigate these drawbacks, heterogeneous catalysis using highly active immobilized palladium catalysts has attracted more and more attentions. The heterogeneous catalysts are often readily removed by simple filtration and recycled several times with no detectable metal leaching.[3-8] These catalysts are generally immobilized palladium species on supports such as activated carbon, alumina, silica, or polymers. Recently, more and more researches have carried out on the environmental-friendly and low cost natural polymers as solid supports.[9-12] Chitosan (CS), N-deacetylation products of chitin, the second most abundant nature biopolymer only to cellulose, has been effectively used as a catalytic support for Pd, Cu, Ni, and so on.[13, 14] The main advantages of CS as a catalyst support are plenty of polar functional groups (amine, carbonyl, carboxyl, amid) having good chelating with transition metals within the molecular backbone and great convenience in preparation into different forms: flakes, gel beads, membranes, fibers and so on. However, several limiting factors of CS as supports could not be ignored: poor thermal stability, mechanical property, and the solvent-resistance. Therefore, CS needs to modify either by chemical or physical methods to improve such properties.

Recently, chitosan-based nanocomposites have attracted more and more attentions. The introduction of nanoscale fillers having at least one dimension in the nanoscale range (such as clay minerals, silica and nano-hydroxyapatite) to chitosan matrix can combine the properties of both organic and inorganic components, such as mechanical properties, thermal behavior, barrier properties, etc.[15-19] Among them, chitosan modified with montmorillonite (MMT, the most used natural clay) composites are of major interests.[20-22] MMT, a kind of natural layered silicates, consist of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide (general structure 2:1 type). The interlayer of MMT contains metal cations, mainly Na^+, Ca^{2+}, or Mg^{2+}, which can be exchanged by other cations including polycationic polymer like CS in slightly acidic condition. Moreover, function groups of CS can form hydrogen bonds with Si-O-Si groups of silicate multilayer and silicate hydroxylated end groups of MMT. Consequently, strong interactions between CS and MMT can easily form, leading to significantly improvements in mechanical, thermal, antimicrobial, and corrosion properties of CS. However, to the best of our knowledge, most of the reported studies of CS/MMT nano-composites are especially for absorbents, tissue engineering, pharmaceutical carrier, food packaging, and etc.[23-27] Few work deal with CS-based/MMT nanocomposite materials as heterogeneous transition metal catalyst supports. In previous work, it was confirmed that CS directly crosslinked by Pd^{2+} cations membrane catalyst was highly active and stable for Heck reactions.[28] Taking these antecedents into account, in this study, CS/MMT nanocomposite microspheres were prepared with a transition metal crosslinker (Pd^{2+}) to form novel high-performance heterogeneous hybrid microsphere catalysts for coupling reactions. The effects of MMT loading amount, intercalation structure, and Pd species dispersion on the morphology, thermal stability, and catalytic performances in Sonogashira type coupling reactions of the hybrid microspheres have been investigated.

Results and Discussion

In this study, FTIR analysis was applied to investigate the interactions between CS, MMT and Pd. As shown in **Fig. 1f**, the FTIR spectrum of CS shows broad bands at 3423 cm^{-1} for overlapping of O-H and N-H stretching, 2923 and 2864 cm^{-1} for aliphatic C-H stretching, 1665 cm^{-1} for C=O stretching of residue amide, 1590 cm^{-1} for N-H bending, 1425 and 1380 cm^{-1} for C-H bending of methylene and methyl groups, 1155 and 1026 cm^{-1} for C-O stretching. In the MMT spectrum (**Fig. 1a**), it was showed that the vibration bands at 3628 cm^{-1} for O-H stretching in the inner surface of MMT, 3445 cm^{-1} assigned to interlayer and O-H stretching of H_2O, 1644 cm^{-1} for O-H deformation of H_2O, 1037 cm^{-1} for Si-O stretching, 907 cm^{-1} for Al-OH vibration, 790 cm^{-1} for Mg-OH vibration, 521 cm^{-1} and 467 cm^{-1} for Si-O bending. Examination of **Fig. 1b-d**, the FTIR spectrum of the CS/MMT/Pd hybrid microspheres showed the combination of characteristic absorption peaks of CS and MMT. And the interactions between the components were reflected by the noticeable wavenumber shifts of the characteristic absorption peaks. The peaks at 1590 cm^{-1} N-H bending of $-NH_2$ groups in the starting CS were shifted to higher wavenumber (1601 cm^{-1}) in the CS/MMT hybrid microspheres. Meanwhile, peaks at 3628 cm^{-1} for O-H stretching in starting MMT and 3423 cm^{-1} of OH and/or NH_2 groups in starting CS were all shifted to lower wavenumber. These bands shifts were related to the electrostatic interactions between CS and MMT, confirming complexation between them. After immobilization of Pd species, the bands around 3400 cm^{-1} region were further shifted to lower wavenumber, meaning complexation reaction of Pd^{2+} with $-NH_2$ and/or -OH functional groups of CS.

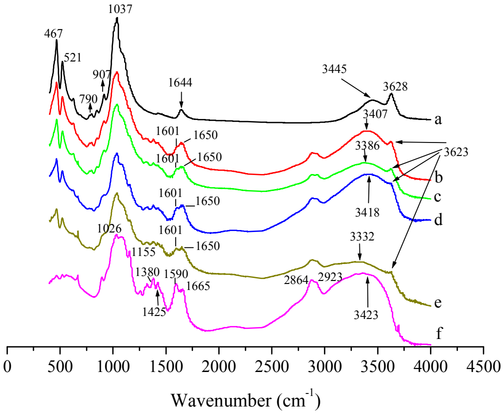


Fig. 1 FTIR curves of the microspheres: a. MMT; b. CS/MMT (50/50); c. CS/MMT/Pd (50/50/1.2); d. CS/MMT (75/25); e. CS/MMT/Pd (75/25/1.2); f. CS.

The structural phases in the hybrid microspheres have been investigated with XRD analysis. As shown in **Fig. 2f**, pure CS XRD diffraction pattern had two broad peaks, one at 2θ=10.37°, the other at 2θ=20.08°. The XRD diffraction pattern of MMT showed a characteristic reflection peak at 2θ=7.06°, corresponding to a basal spacing d_{001} of 1.26 nm. Incorporating MMT within CS matrix leaded to a shift in the basal peak from 2θ=7.06° to 6.19° (CS/MMT: 75/25, **Fig. 2d**) and 5.44° (CS/MMT: 50/50, **Fig. 2b**). The corresponding basal spacing d_{001} were 1.43 nm and 1.62 nm, respectively. This increase in d-spacing indicated the formation of intercalated structure of CS/MMT hybrid microspheres. As proven in FTIR analysis, amino and hydroxyl groups of CS could form hydrogen bonding with silicate hydroxylated end groups of MMT, leading strong interactions between CS and MMT. Hydroxyl groups of CS also could form hydrogen bonding with Si-O-Si groups of silicate multilayer of MMT. Moreover, NH_2 groups of CS have converted to $NH_3^+Ac^-$ in acidic media. Therefore, CS molecules can easily go inside the interlayers of MMT and form intercalated structure through the cations exchange process. As shown in **Fig. 2c, 2e**, the addition of Pd^{2+} has little influences on the intercalation between CS and MMT. It means that the added Pd^{2+} cations mainly form complexation reactions with CS molecules not MMT.

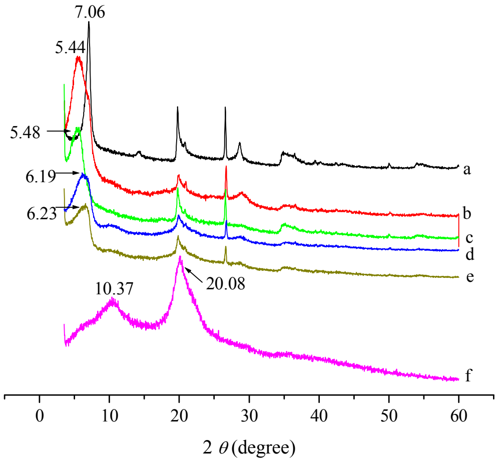


Fig. 2 XRD curves of the microspheres: a. MMT; b. CS/MMT (50/50); c. CS/MMT/Pd (50/50/1.2); d. CS/MMT (75/25); e. CS/MMT/Pd (75/25/1.2); f. CS.

The thermal stability of pure CS microspheres, MMT, and CS/MMT hybrid microspheres has been investigated with TG analysis under air atmosphere (as shown in **Fig. 3**). The TGA curve of pure CS microspheres showed a weight loss in three stages. The first stage (50-130 °C) was attributed to the loss of absorbed and bound water. The second stage (180-350 °C) due to the destruction of the intermolecular interactions such as hydrogen bonding, crosslinking, destruction of the macromolecular backbone, carbonization, and thermal oxidation. The third stage (370-500 °C) due to the carbonization, and deep thermal oxidation. Pure MMT exhibited high thermal stability containing only one weight loss stage (50-110 °C) caused by the evaporation of the absorbed water. After incorporating MMT within CS matrix, it is showed that the thermal stability of CS/MMT hybrid microspheres was improved obviously with MMT amount increasing. The nano-dispersed MMT in the CS matrix leaded to significant delay in weight loss as compared with pure CS, especially at high temperature (>300 °C). At 80% weight residue is concerned, the decomposition temperature of CS/MMT hybrid microspheres (277.9 °C) was 27.4°C higher than pure CS microspheres (250.5 °C). At 60% weight residue is concerned, the decomposition temperature of CS/MMT hybrid microspheres (75/25: 361.3 °C; 50/50: 510.4) got a step further higher than pure CS microspheres (305.3 °C). The added MMT formed strong interactions with CS molecules and acted as good thermal barriers for CS matrix. Therefore, thermal stability of CS matrix was improved effectively with addition of MMT. This is in favour of the improvement of the resistance to harsh reaction conditions when CS/MMT hybrid microspheres used as catalyst supports materials.

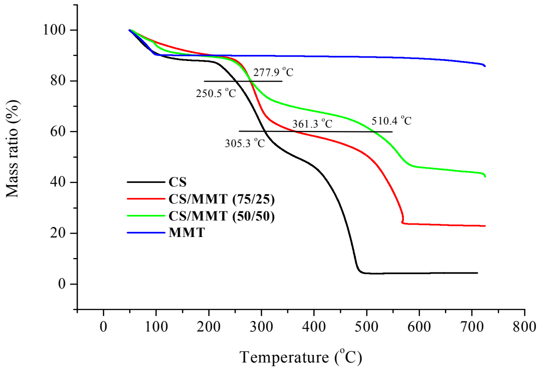


Fig. 3 TGA curves of the microspheres supports.

SEM is often used to study the morphology of polymeric composites. The SEM photos of the surface and cross-section of the hybrid microspheres with different magnification were shown in **Fig. 4**. For all the CS/MMT/Pd hybrid microspheres with different MMT amount, the interfaces between MMT domain and CS matrix had a rough structure, indicating good interfacial interaction between MMT and CS. MMT particles dispersed well within CS matrix sized in about 5 μm. No agglomerates in larger size observed with increasing MMT amount. These phenomenons indicated fairly good miscibility between CS and MMT.

The nano-sized microstructure of the CS/MMT/Pd hybrid microspheres was further investigated with HR-TEM analysis. Previous study [28] has showed that Pd species immobilized on CS supports would undergo a valence transform cycle (Pd^{2+} to Pd^0 to Pd^{2+}) during the catalytic cycle as applied in coupling reactions. In HR-TEM study, both fresh and activated CS/MMT/Pd hybrid microspheres (reduced with alcohol) have been investigated. As shown in **Fig. 5,** HR-TEM image of fresh CS/MMT/Pd hybrid microsphere showed the good dispersion of MMT with intercalated structure (stacks of multilayers) in CS matrix. Meanwhile, no individual separated Pd species were found for the fresh CS/MMT/Pd hybrid microspheres, suggesting that Pd^{2+} cations dispersed in molecular level. In the case of the activated CS/MMT/Pd hybrid microspheres, individual separated Pd^0 nanoclusters sized about 5 nm dispersed well both in CS matrix and interlays of MMT. The valence changing of Pd can be confirmed with the XPS analysis and the colour change of the CS/MMT/Pd hybrid microspheres. After activated, the CS/MMT/Pd hybrid microspheres had a characteristic color change from pale yellow to gray, meaning some Pd^0 species generated. As shown in **Fig. 6**, the Pd $3d_{5/2}$ electron binding energy of the fresh CS/MMT/Pd hybrid microspheres was mainly at 337.8 eV, meaning mainly Pd^{2+} species in the materials. After activated, besides at 337.8 eV, Pd $3d_{5/2}$ electron binding energy was also found in 334.6. And the peak at 336.1 became stronger. These results indicated both Pd^{2+} and Pd^0 species coexisting within the CS/MMT/Pd hybrid microspheres after activated with alcohol.

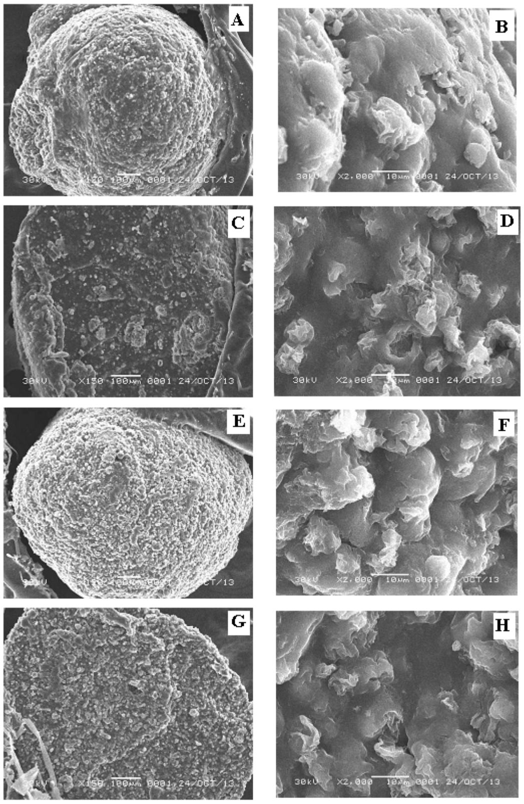


Fig. 4 SEM observation of the CS/MMT/Pd hybrid microspheres with different magnifition: A. CS/MMT/Pd (75/25/1.2), surface, (×150); B. CS/MMT/Pd (75/25/1.2), surface, (×2000); C. CS/MMT/Pd (75/25/1.2), cross section, (×150); D. CS/MMT/Pd (75/25/1.2), cross section, (×2000); E. CS/MMT/Pd (50/50/1.2), surface, (×150); F. CS/MMT/Pd (50/50/1.2), surface, (×2000); G. CS/MMT/Pd (50/50/1.2), cross section, (×150); H. CS/MMT/Pd (50/50/1.2), cross section, (×2000).

Combining the characterization results of the prepared CS/MMT/Pd hybrid microspheres, mechanism of the formation of interactions between CS, MMT, and Pd species has been proposed at **Scheme 1**. CS has good miscibility with MMT and can easily intercalate into the interlays of MMT by cationic exchanging process. Pd^{2+} cations form strong complexions with functional groups of CS (mainly $-NH_2$ group). Pd^{2+} cations can be reduced to Pd^0 and form nanoclusters entrapped within CS matrix and located between interlays of MMT.

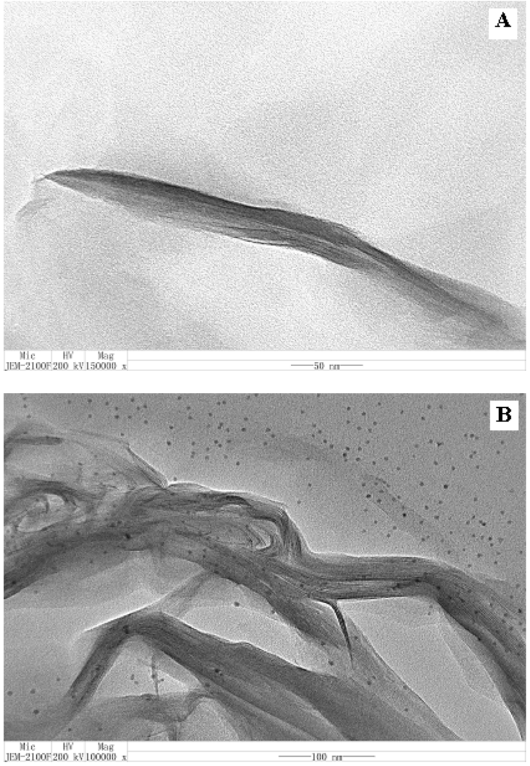


Fig. 5 HR-TEM observation of the microspheres: A. CS/MMT/Pd (75/25/1.2), fresh; B. CS/MMT/Pd (75/25/1.2), after activated.

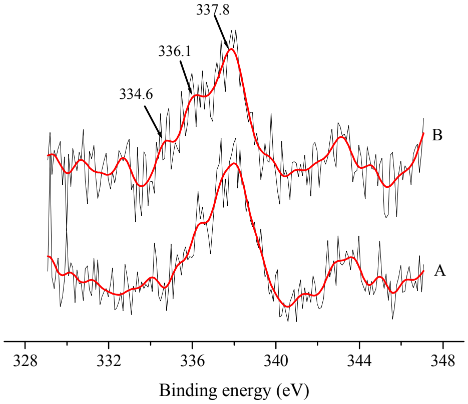
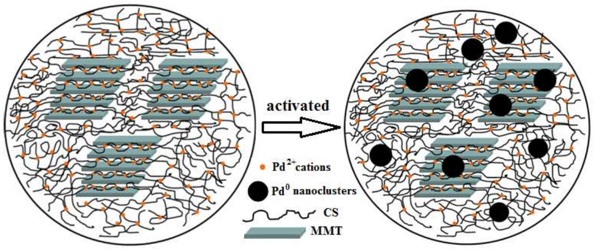


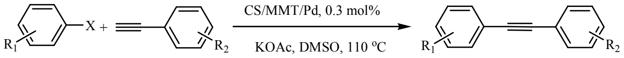
Fig. 6. XPS analysis results of the microspheres: A. CS/MMT/Pd (75/25/1.2), fresh; B. CS/MMT/Pd (75/25/1.2), after activated.



Scheme 1. Phase dispersion diagram of the fresh and activated CS/MMT/Pd hybrid microspheres.

The Sonogashira reaction is known as the most powerful and straightforward method for the construction of the sp^2-sp carbon-carbon bonds [29-31]. Similar activity for the reaction of iodobenzene with phenyl acetylene (as shown in **Fig.1S** of the ESI) was found between the CS/MMT/Pd (75/25/1.2) and CS/MMT/Pd (50/50/1.2) catalysts. Therefore, one catalyst (CS/MMT/Pd (75/25/1.2)**)** was chosen to assess the catalytic activities for Sonogashira coupling reactions of other aryl halides with alkynes. Examination of **Table 1** shows that over 90% crosscoupling yield can be achieved for the reaction of iodobenzene with substituted phenyl acetylenes (entry 1-3) as the CS/MMT/Pd (75/25/1.2) catalyst loading is 0.3 mol%. Our catalyst loading is clearly much lower than recent reported Pd/PVA mats catalysts for the same reaction [32], indicating excellent catalytic activities of the CS/MMT/Pd hybrid microspheres catalyst for the Sonogashira-type cross-coupling reactions. Such good catalytic activity should be much related to the well dispersion of Pd species [33, 34] (Pd^0 sized about 5 nm) in the composite microsphere. Smaller size of Pd^0 species was in favor of the higher catalytic performance for reactions.[33] The CS/MMT/Pd hybrid microspheres catalyst also works well for other aromatic iodides coupling with alkynes. High cross-coupling yield occurred in the substituted aromatic iodides either with an electron-donating group such as *o*-OCH$_3$ (entry 4), *p*-OCH$_3$ (entry 5), *p*-CH$_3$ (entry 6) or with an electron-withdrawing group such as *o*-Cl (entry 7), *p*-F (entry 8). It is found that the substituted group's steric effects of the reaction substrates have a bit influence to the yield. For example, the cross-coupling yield of entry 4 is clearly lower than that entry 5, due to such steric effects of ortho substituted substrates (*o*-OCH$_3$) than para substituted substrates (*p*-OCH$_3$). The CS/MMT/Pd hybrid microspheres catalyst has low activity for bromobenzene with alkynes (entry 9), due to the greater strength of the C-Br bond than of the C-I bond. Most of other reported polymer supported Pd heterogeneous catalysts also has low activities for aryl bromides entering cross-coupling reactions with no addition of any ligands.[32, 34-36]

Table 1. Sonogashira cross-coupling of various aromatic halides with alkynes catalyzed by CS/MMT/Pd hybrid microspheres [a].



Entry	Aromatic Halide	Alkyne Substrate	Cross-coupling Yield (%) [b]
1	C_6H_5I	C_6H_5CCH	94
2	C_6H_5I	4-$CH_3OC_6H_4CCH$	90
3	C6H5I	4-CH_3C6H_4CCH	92
4	2-$CH_3OC_6H_4I$	C_6H_5CCH	69
5	4-$CH_3OC_6H_4I$	C_6H_5CCH	88
6	4-$CH_3C_6H_4I$	C_6H_5CCH	85
7	2-ClC_6H_4I	C_6H_5CCH	78
8	4-FC_6H_4I	C_6H_5CCH	92
9	C_6H_5Br	C_6H_5CCH	trace

[a] Reaction conditions: 1 mmol aromatic halide, 1.2 mmol alkyne, CS/MMT/Pd (75/25/1.2) hybrid microspheres (0.026g, containing 3 μmol Pd), 3 mmol base (CH_3COOK), in 3+0.2 ml (DMSO+ethylene glycol) solvent, at 110 °C for 5 h.[b] GC/MS yield.

In this study, the prepared CS/MMT/Pd hybrid microspheres catalyst has a big size in diameter (about 1.2 mm) and it can be easily filtrated out from the reaction medium and reused for next reaction runs. Sonogashira coupling of iodobenzene with phenyl acetylene was employed as the model reaction to assess the stability and reusability of the CS/MMT/Pd hybrid microspheres catalyst. As shown in **Fig. 7**, the novel catalyst can be recycled 10 times without significant decrease in coupling yields, indicating higher stability than other reported heterogeneous polymer supported palladium catalysts for Sonogashira reactions, such as palladium-poly(3-aminoquinoline) hollow sphere composite (3 times) [34], and $PdCl_2$ on modified poly(styrene-co-maleic anhydride) (5 times) [35]. The main reason of the higher stability of the prepared CS/MMT/Pd hybrid microspheres catalyst should be attributed to the following facts. Firstly, the CS/MMT/Pd hybrid microspheres catalyst has much higher mechanical strength and thermal stability than those of palladium-poly(3-aminoquinoline) oligomer catalyst for its much higher molecular weight of the matrix CS macromolecules. Secondly, the complexation of Pd species with S, N within thiazole groups, and -C=O groups in the case of modified poly(styrene-co-maleic anhydride) supported Pd catalyst are much weaker than those formed from Pd species with $–NH_2$ groups, -OH groups within each repeat units of CS molecular backbone in the case of the CS/MMT/Pd hybrid microspheres catalyst. For comparing, with similar palladium catalyst loading amounts, the CS/MMT/Pd hybrid microspheres catalyst has clearly much better recyclability than pure CS/Pd microspheres catalyst (6 times). Meanwhile, it is also found that the yield of the last 2 recycling runs in the case of CS/MMT/Pd (50/50/1.2) hybrid microspheres catalyst is higher than CS/MMT/Pd (75/25/1.2) hybrid microspheres catalyst. These results mean that the addition MMT is great beneficial to the improvements of the stability and reusability of the CS-base supported palladium catalysts.

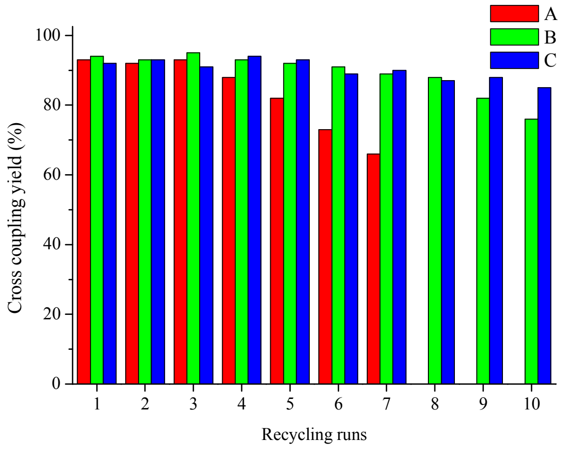


Fig. 7 Dependence of the cross-coupling yield on the recycling runs of the microspheres catalysts as used in model Sonogashira reaction: A. CS/Pd (100/1.2) microspheres; B. CS/MMT/Pd (75/25/1.2) hybrid microspheres; C. CS/MMT/Pd (50/50/1.2) hybrid microspheres.

For heterogeneous catalysts, transition metal leaching is known as the main reason that caused the declining in the catalytic activity with the increase of the recycling times. [37] The Pd content of the freshly prepared as well as the recycled heterogeneous catalysts has been determined by means of ICP. As shown in **Fig. 8**, Pd leaching percent is much slower in the CS/MMT/Pd hybrid microspheres catalyst than pure CS/Pd microspheres catalyst. And it is also found that Pd leaching in the case of CS/MMT/Pd (75/25/1.2) hybrid microspheres catalyst is slightly serious than that of CS/MMT/Pd (50/50/1.2) hybrid microspheres catalyst. The higher Pd leaching-resistance properties of the CS/MMT/Pd hybrid microsphere catalysts should be mainly attributed to the effectively improvements in the mechanical and thermal stability of the composite microspheres after incorporation of MMT. Moreover, the formation of strong interactions involved in CS molecules, MMT layers, and Pd species is also in great favor of the reducing in Pd leaching.

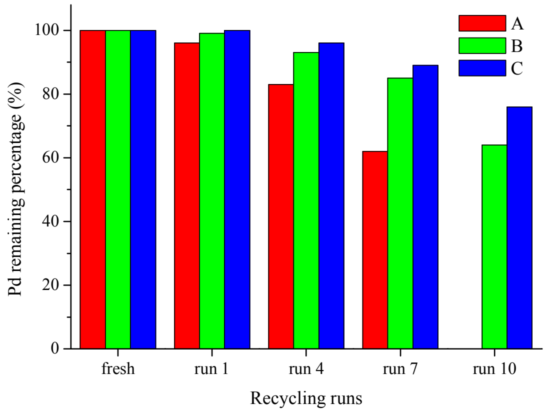


Fig. 8 Dependence of the Pd retaining percentage on the recycling runs of the microspheres catalysts as used in model Sonogashira reaction: A. CS/Pd (100/1.2) microspheres; B. CS/MMT/Pd (75/25/1.2) hybrid microspheres; C. CS/MMT/Pd (50/50/1.2) hybrid microspheres.

Conclusions

In summary, it has been demonstrated that CS combination with MMT produced a very good catalyst support for stabilizing palladium, decreasing drawbacks of CS itself. CS molecules can easily intercalate into the interlays of MMT by cationic exchanging process, leading to good miscibility of the CS matrix and MMT. Pd^{2+} cations acted as a metal crosslinker for CS molecules both in matrix and interlays of MMT. The reduced Pd^0 nanoclusters sized 5 nm entrapped tightly within CS matrix and interlays of MMT. Therefore, the thermal stability and Pd leaching-resistance of the CS/MMT/Pd hybrid microsphere catalyst was improved effectively. And noticeable enhancement of the catalytic stability and activity was obtained. Both CS and MMT are natural abundant and cheap to obtain. The inexpensive and environmental friendly CS/MMT/Pd hybrid microsphere catalyst might be a good candidate heterogeneous palladium catalyst for organic reactions.

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Notes and references

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