

(CTA)₂S₂O₈ as Self-Decomposed Soft Templates

Tianyou Chen, Binyang Du, Zhiqiang Fan

Brief Introduction

Organic-inorganic hybrid mesoporous polymers were successfully synthesized by using a templatedirected free radical polymerization technique in aqueous solution at 0-5 °C with oxidative complexes as self-decomposed soft templates. The oxidative complexes ($(CTA)_2S_2O_8$), which were formed between anionic oxidant $(S_2O_8^{2-})$ and cationic surfactant (cetyl trimethylammonium bromide, CTAB) at 0-5 °C, can be automatically decomposed due to the reduction of $S_2O_8^{2-}$. No additional treatment was needed to remove the templates. The reactive functional monomer, 3-(trimethoxysilyl)propylmethacrylate (TMSPMA), was used as main monomer. Styrene was used as the co-monomer. With simultaneous free radical copolymerization of TMSPMA and styrene, condensation of methoxysilyl groups and the selfdecomposition of $(CTA)_2S_2O_8$, organic-inorganic hybrid mesoporous polymers were successfully obtained. The mesoporous structures and morphologies of the resultant hybrid mesoporous polymers were found to be strongly dependent on the feed amounts of TMSPMA and styrene. In the absence of styrene, the hybrid polymer PTMSPMA exhibited mesh-like bicontinuous structures with mesopores and high surface area (335 m²/g). With the incorporation of styrene, mesoporous nanoparticles were obtained. The surface areas of the mesoporous nanoparticles decreased with the increasing of styrene contents. The adsorption capabilities of such mesoporous polymers for organic dye (congo red) and protein (bovine serum albumin) were also studied.



Si-OH

Scheme 1. Schematic illustration of the structure and chemical property of the organic-inorganic hybrid mesoporous PTMSPMA.

Fabrication and Characterizations





 \mathcal{O} CTA⁺ ion $\bigcirc S_2O_8^{2-}$ ion \mathcal{O} TMSPMA molecule $(CTA)_2S_2O_8$ template TMSPMA droplet Mesoporous PTMSPMA

Scheme 2. The schematic illustration of the preparation process of mesoporous PTMSPMA.



Figure 1. TEM images of the resultant mesoporous polymers. (a) PTMSPMA, (b) PTS-15, (c) PTS-5, and (d) PTS-2.



Figure 2. SEM images of the resultant mesoporous polymers. (a) PTMSPMA, (b) PTS-15, (c) PTS-5, and (d) PTS-2.

Figure 3. FT-IR spectra of the resultant hybrid mesoporous polymers, i.e. PTMSPMA, PTS-15, PTS-5, and PTS-2.

Table 1. The feed amounts of the monomers (TMSPMA and styrene) and the porous properties of the resultant organic-inorganic hybrid mesoporous polymers.

Sample codes	Feed amounts /mL		Porous properties	
	TMSPMA	Styrene	BET surface area (m ² /g)	Pore volume (cm ³ /g)
PTMSPMA	1.50	/	335	0.610
PTS-15	1.50	0.10	170	0.503
PTS-5	1.50	0.30	132	0.442
PTS-2	1.50	0.75	82	0.237



Figure 4. (a) Nitrogen adsorption-desorption isotherms of PTMSPMA, PTS-15, PTS-5, and PTS-2. (b) Barret-Joyner-Halenda (BJH) pore size distributions calculated from the corresponding desorption data in (a).



Applications



Figure 5. The UV spectra of filtered mixed solutions after mixing PTS-2, PTS-5, PTS-15, and PTMSPMA, respectively, in the 50 mg/L congo red(CR) aqueous solutions for 24 hrs.

Figure 6. Adsorption isotherm fitted with Langmuir (black line), Freundlich (red line), Redlich-Peterson (green line), and Tempkin (blue line) models for the adsorption of mesoporous PTMSPMA in BSA acetate buffer solutions at room temperature.

Conclusions

Organic-inorganic hybrid mesoporous polymers were successfully synthesized by using a template-directed free radical polymerization technique with oxidative complexes $(CTA)_2S_2O_8$ as self-decomposed soft templates. The surface areas of the mesoporous nanoparticles decreased with the increasing of styrene contents. Such organic-inorganic hybrid mesoporous polymers may be used in the adsorption or separation of congo red and BSA.

References

(1).Langmuir, I., The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. J. Am. Chem. Soc. 1918, 40, 1361-1403. (2). Freundlich, H., Concerning Adsorption in Solutions. Z. Phys. Chem. Stoechiom. Verwandtschafts. 1906, 57, 385-470. (3).Redlich, O.; Peterson, D. L., A Useful Adsorption Isotherm. J. Phys. Chem. 1959, 63, 1024-1024. (4). Tempkin, M.J.; Pyzhev, V., Kinetics of Ammonia Synthesis on Promoted Iron Catalysts. Acta Physicochim. URSS. 1940, 12, 217-256.

The authors thank the National Natural Science Foundation of China for financial support.