Synthesis, Characterization and Application of Large Pore Cubic Mesostructured Silica Materials

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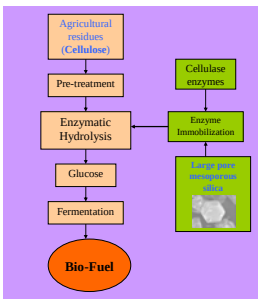
Introduction



The major hindrance of enzyme commercially application is the high cost of enzyme which is caused by low stability of enzyme. Enzyme stability can be improved through various methods, i.e. *enzyme immobilization*, enzyme modification, protein engineering and medium engineering.

Mesoporous silicas have many advantages such as narrow pore size distribution, tunable pore size and the possibility to modify surface characteristics, which makes them promising applications as supports for bio-molecule adsorption.

Large pore cubic mesostructured silica materials **have a great potency as supporting materials for enzyme immobilization. The cubic mesostructured (cage like materials) is basically a large cavity with many entrance pores. Comparing to 1D channel system like MCM-41, the 3D pore system shows superiority in terms of mass diffusion or mass transfer.**

In this review we report the functionalization of large pore mesoporous silica with cage like structure using a co-condensation method. Different organosilanes (APTES, MPTMS, VTMS and PTMS) were used for the surface modification. In order to create a very large pore, low temperature synthesis and high hydrothermal temperature methods were used. The synthesized materials (functionalized silica and pure silica) were used in *Celulase enzyme immobilization*.

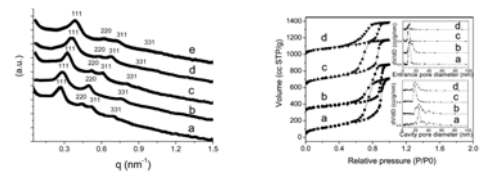
Experimental

Synthesis of Mesoporous Silica
The synthesis of mesoporous silica follows the LP-FDU-12 method [1,2] With the composition of reactants: TEOS/F127/TMB/KCl/HCl/H2O is 1.00/0.0037/0.50/3.36/6.00/155 (molecular composition)
a. Stirring/Synthesis
1 gr F127 is mixed with 5 gr KCl and 60 ml of 2 M HCl in the beaker with the temperature is kept on 15 C. After 15 minutes 1.2 gr of TMB was added into the solution. The next step was adding 4.16 gr of TEOS into the solution. Then the stirring continued for 24 hr. During the stirring the temperature remained 15 c continuously.
b. Hydrothermal treatment
All the solution then removed to an autoclave then heated at certain high temperature for 72 hrs (3 days),
c. Removing the template
The dried samples are washed with 250 ml of ethanol and 2 ml of HCl at 60 C, three times for 6 hr each.

Synthesis of Functionalized Mesoporous Silica
The basic process is the same with LP-FDU. The difference is when added TEOS in the solution, certain amount of functional organic also added to the solution. The composition of other components (F127/TMB/KCl/HCl/H2O) is kept constant.

Results & Discussion

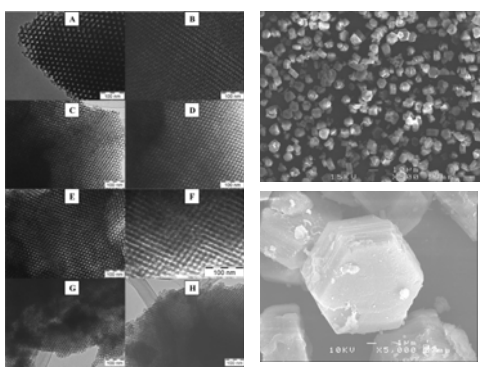
Characterization (SAXS, N_2 sorption)



SAXS analysis (a: pure silica; b: APTES; c: VTMS; d: MPTMS; e: PTMS) and N2-sorption isotherm (a: APTES; b: VTMS; c: MPTMS; d: PTMS)

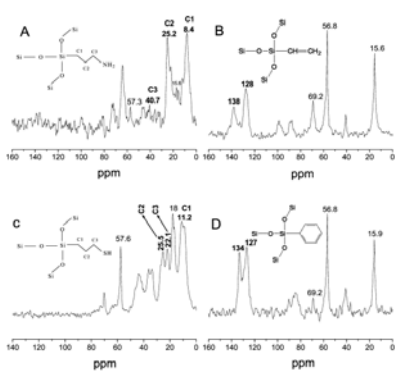
- The SAXS spectrum reflect an ordered face-centered cubic (fcc) structure. The nitrogen sorption isotherms in agreement with the SAXS analysis indicate the presence of mesoporous structure with cage like structure.

SEM and TEM images of MSNs



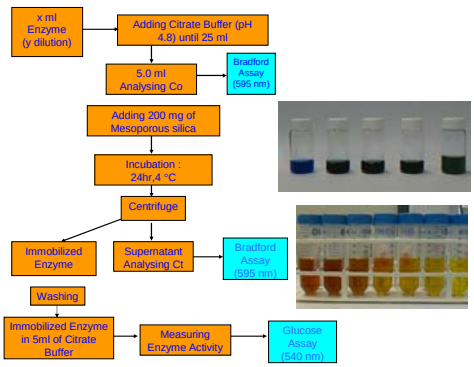
- TEM images of (A,B) APTES; (C,D) VTMS; (E-F) MPTMS and (G,H) PTMS. SEM images of APTES

13C-CP-MAS-NMR



- 13C solid state cross-polarization magic-angle spinning nuclear resonance spectra of (A) APTES, (B) VTMS, (C) MPTMS, (D) PTMS

Enzyme immobilization and catalysis



Enzyme Loading and Activity

sample	loading capacity, q_m (mg of cellulase/ g of silica)	enzyme activity (U/mg of enzyme)
free cellulase		14.00
pure silica	4.35	1.64
	4.60	1.34
	6.71	10.55
	7.92	10.75
	8.55	9.98
	11.75	10.49
S-VTMS	7.38	9.86
	12.63	10.36
	16.69	10.50
	17.05	10.94
	17.55	11.24
S-APTES	1.60	0.48
	5.54	0.53
	15.99	1.09
	16.12	1.10
	19.05	2.18

Conclusions

1. Organo functionalized FDU-12 type silicas exhibiting large pore sizes and ordered mesoporous structures have been synthesized at low reaction (15ºC) and high hydrothermal temperatures (160ºC) via the co-condensation method.

2. Enzyme immobilization efficiency, activity and stability varied significantly with organic functionality due to size exclusion effects, electrostatic and hydrophobic interactions between the organo-functionalized surfaces and the enzymes.

3. Cellulase immobilization on vinyl (VTMS) functionalized FDU-12 mesoporous silica appeared to be the most promising approach, since it occurred with high efficiency, maintained enzyme activity, and provided temporal enzyme stability.

References:

[1]. Sandy Budi Hartono, Shizhang Qiao, Kevin jack, Bradley P. Ladewig, Zhengping Hao and Gao Qing Max Lu. Langmuir, 2009. 25 (11), 6413-6424
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[3]. Fan, J., et al., Cubic mesoporous silica with large controllable entrance sizes and advanced adsorption properties. Angewandte Chemie, International Edition, 2003. 42(27): p. 3146-3150;
[4]. Fan, J., et al., Low-temperature strategy to synthesize highly ordered mesoporous silicas with very large pores. Journal of the American Chemical Society, 2005. 127(31): p. 10794-5

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