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Double-Mesopore V-MSU-X Silica and its Pure Siliceous Derivative Prepared by One Synthesis System

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Abstract: Non-ionically templated organo-modified MSU-2 mesoporous silicas have been prepared in neutral medium by co-condensation TEOS and vinyltriexoylsiloxane (VTES) and exhibit highly symmetric bimodal mesopore systems. A bromination reaction of V-MSU-2 provides evidence for attachment of most vinyl groups to the accessible surface within the channels. Further, siliceous MSU-2 materials with double pore size have been obtained from calcination of so-produced organo-modified MSU-2 and demonstrate the immense flexibility of the non-ionic templating system.

Keywords: Organically modified MSU-X, double pore systerm, mesoporous materials.

Since their first disclosure of the M41S family of materials[1,2] in 1992, considerable research effort has been developed to prepare the other derivatives of mesoporous materials such as SBA[3] and MSU-X[4,5] silicates by using different polymeric and oligomeric templates. The later involved different sorts of nonionic poly (ethylene oxide)-based surfactants, which led to the family of MSU-X (X=1-4) and then provided new advantages in either topologies or processing. The interest in these materials arises from the advances that the texture could easily be tailored by varying preparation parameters[4-10].

However, materials with bimodal pores are of considerable interest for applications in catalysis and separation because they offer multiple benefits arising from each pore size regime[10]. For instance, while micro and meso-pores may provide size- or shape-selectivity for guest molecules, the presence of additional macropores can offer easier transport and access to the active sites that should improve reaction efficiencies and minimize channel blocking.

Here we simultaneously created inorganic-organic hybrid mesostructures consisting of a bimodal pore system from non-ionic alkyl-aryl EO_{15} surfactant ($C_8H_{17}(C_6H_4)(EO)_{15}H$, denoted Tx-15) and thereby used these to obtain siliceous MSU-2 by the simple removal of the organic groups upon programmed calcinations. We report, for the first time, the synthesis of vinyl functionalized MSU silica (V-MSU-2) and their derivatives of siliceous MSU-2 with double pore diameters. A bromination reaction of V-MSU-2 provides evidence for attachment of most vinyl groups to the accessible surface within the channels.

The x-ray patterns (see **Figure.1**) are used to elucidate the structure of the surfactant-extracted vinyl functionalized MSU silica (V-MSU-2) with VTES/TEOS ratio of 0.1 and its derivatives after calcinations or bromination. The observation of single XRD reflection is a symbol of the pore structure based on a three-dimensional network of worm-like porous channels arrays. This arrangement is characteristic of the recently prepared MSU compounds[4,5]. The bimodal pore framework is highly thermal stable up to 850°C at least for two hours without damaging the double pore structure. The d_{100} spacings of the derivatives decreased comparable to their primary product as the vinyl-modified material was calcined at given temperature (550 and 850°C respectively) or that was brominated (the product denoted BE-MSU-2, see **Table 1**). Unlike usual MSU-X, the present materials have large d_{100} spacings (see **Table1**), which was very close to that in double pore size [Si]-MSU-X[6] (7.54 nm). This result gave an initial hypothesis that the XRD reflections resulted from a novel pore structure. Further studies suggested that the structure simultaneously possessing two distinct pore arrangements.

The symmetric bimodal mesopore structure was supported by N_2 adsorption isotherms and corresponding BJH[12] pore size distribution of a representative sample (inset) (see **Figure 2**), which clearly displayed two distinct capillary condensation steps. Nevertheless, the pore size distribution revealed two pore diameter maxima at 3.15 and 40.15 nm (see **Table 1**). Two separate condensation steps are observed on the isotherms. The first one is similar to that for usual MSU, though not very steep. This was attributable to a slight pore size of the sample with a pore diameter maxima 3.15 nm. This is in agreement with the XRD results, *i.e.* broad lines are observed. However the second condensation step on the isotherm at P/P_0 >0.8 is much steeper than the first, indicating the presence the significant amount of secondary mesopores maxima at 40.15 nm. Further evidence for the wormhole framework pore structure of the sample is provided by the transmission electron microscopy (TEM). The mesopores are present as a 'homogenous' mixture through out the entire sample. The pore size is close to the smaller pore distribution in the materials and the larger mesopores are not observed because of it beyond the scale. It is believed that the large one is similar to those present in amorphous mesoporous silica gels, being formed by the packing of small silica particles.

Solid state ^{13}C CP MAS NMR spectra confirmed the presence of vinyl groups. The spectrum showed three resonances for surfactant-extracted V-MSU-2, corresponding to vinyl carbons at 128.7 and 136.0 ppm and ethanol (solvent) at 70.4 and 58.2 ppm *vs* TMS. After several days bromination these peaks disappeared, but a new broad peak at 32.8ppm appeared being indicative of the presence of C-Br bonds. UV-Raman give further support of it, showing the elimination of the C=C stretching mode at 1618cm-1 and appearance of new peaks assigned to C-C and C-Br stretching modes.

Solid state ^{29}Si CP MAS NMR also provides the information about both the silicon environment and the degree of organic functionalization. Siliceous MSU-2 exhibited two main resonances at -102.5 and -112.4 ppm, corresponding to Q^3 $[(SiO)_3Si\text{-}OH]$ and Q^4 $[(SiO)_4Si]$ silicate species, respectively. Upon modified MSU-2 with vinyl groups, the ^{29}Si NMR spectrum showed two additional resonances at -79.9 and -70.3 ppm that assigned to T^3 $[R(SiO)_3Si]$ and T^2 $[R(SiO)_2Si\text{-}OH]$, suggesting that vinyl groups incorporated in the wall surfaces.

SEM image for V-MSU-2 or BE-MSU-2 showed the aggregation particles with uniform distribution in size less than 0.3 micrometers. More aggregated particles were observed after the calcination of V-MSU samples, and higher temperature give slightly larger agglomerations that appear to be amorphous. Differing from normal amorphous porous silica, the particles in the present silica material contain novel pore arrays, responsible for the XRD reflection in 7.32 nm. Using alkyl-PEO

Figure 1 XRD patterns of V10-MSU-2 a. extracted, b. Bromine addition of a, c. a calcined at 550°C and d. at 850°C. The pattern was recorded on a D/MAX-rA diffractometer with Cu-Ka radiation 30KV/30mA.

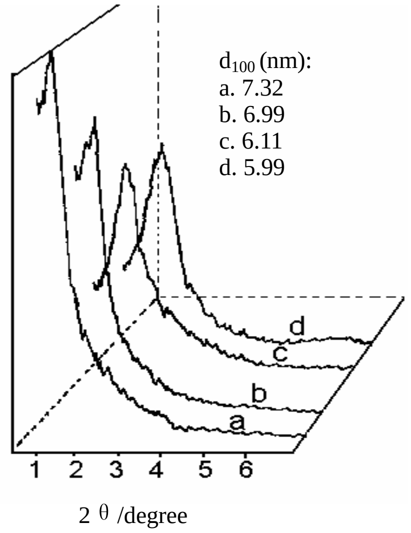
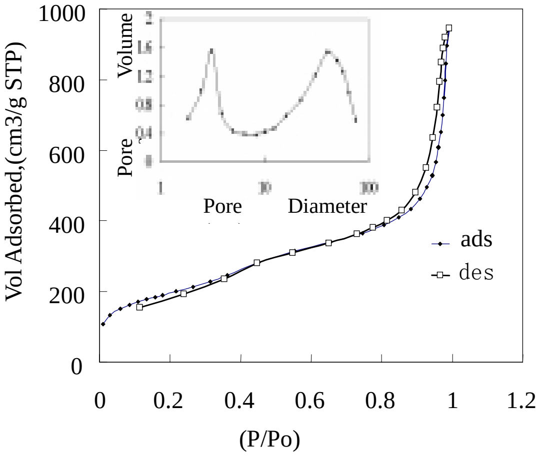


Figure.2 N_2 adsorption-desorption isotherms and pore size distribution for MSU-2 derivative calcined at 550℃



([$C_{12-15}H_{25-31}(EO)_9H$] as the surfactant, only the usual derivatives with single characteristic pore distribution were obtained upon N_2 adsorption analysis. This suggests that both the hybrid precursor and surfactant play important roles in the co-hydrolysis and co-condensation process, *i.e.* the altered organization of the surfactant and hydrogen bond between the hybrid precursor and surfactant finally led to the novel bimodal pore mesostructure. The formation mechanism is under investigations and will be discussed in future contribution.

Table 1 Properties of V-MSU-2 and siliceous MSU-2 silica samples

Samples[*]	VTES/TEOS ratios	d_{100}/nm	BJH[b] Pore Diameter/nm	BET Surf. Area/m^2g^{-1}	Pore Volume/cm^3g^{-1}
1	0.10	7.32	2.99, 42.03	804	1.40
2(cal-550)	0.10	6.11	3.15, 40.15	689	1.23
3(cal-850)	0.10	6.00	2.65, 46.67	425	0.94
4(BE-MSU-2)	0.10	6.99	3.21, 53.18	627	1.15

[a] All samples templated with non-ionic alkyl-aryk EO_{15} surfactant. Sample 2, 3 was obtained by calcining the sample 2 at 550 and 850°C, respectively. Sample 4 was the sample after brominatioon reaction with sample 2.

[b] BJH modal has recently been shown to underestimate pore diameters by up to 20%[13]

In summary, vinyl functionalized MSU-2 and Siliceous MSU-2 with two distinct pore arrangements have been synthesized in one synthesis procedure. The new routes reported here offer a promising alternative approach for production of inorganic-organic hybrid MSU type porous materials and pure siliceous consisting of bimodal pore system. The other precursors proved to be more challenging, such as in the reaction mixture containing methyl or phenyl along TEOS precursors, siliceous double pore size distributions on N_2 adsorption is easily obtained by varying the amount of the ratios of RTES/TEOS. The results briefly outlined here provide further indication of the immense flexibility of the non-ionic alkyl-aryl-PEO templating system. The results show that simple engineering of the chemistry in the synthesis medium can have profound effects on the templating mechanism and resultant porous products.

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