

## ***Supporting Information***

### **Synthesis of Hierarchically Porous Silicas with Mesophase Transformations in Quadru-Component Microemulsion-Type System and the Catalytic Performance for Dibenzothiophene Hydrodesulfurization**

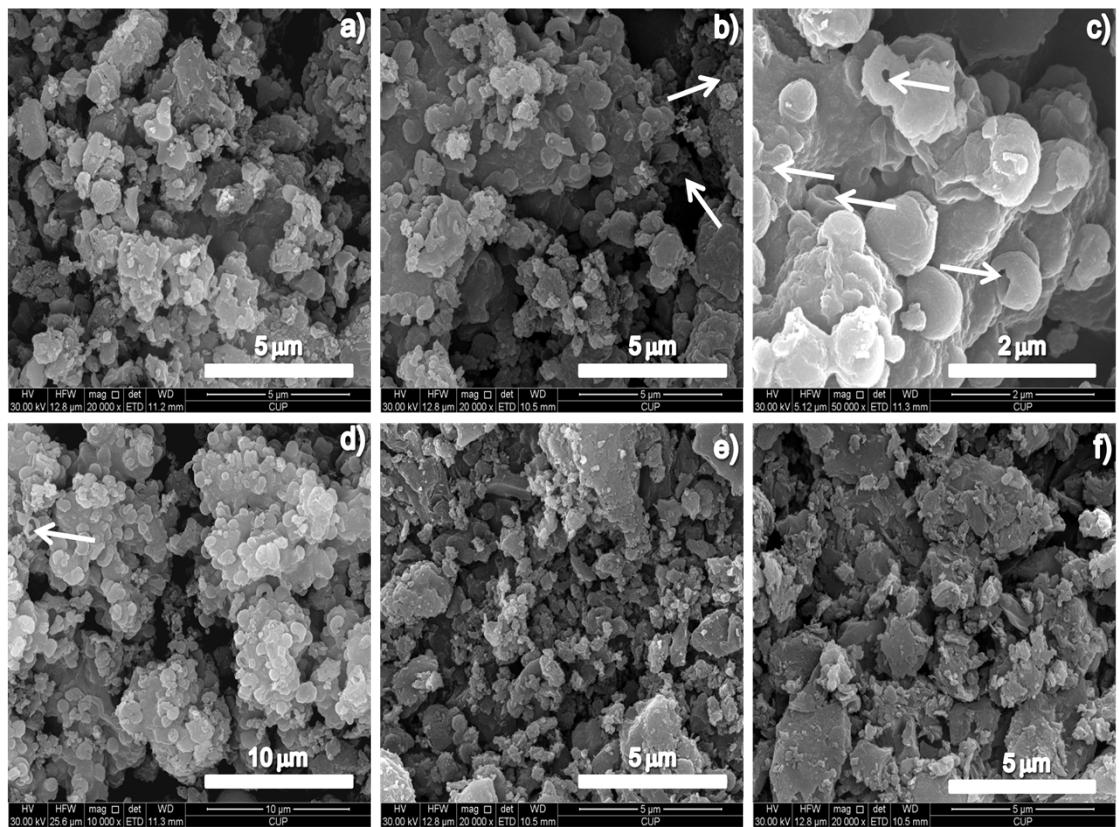
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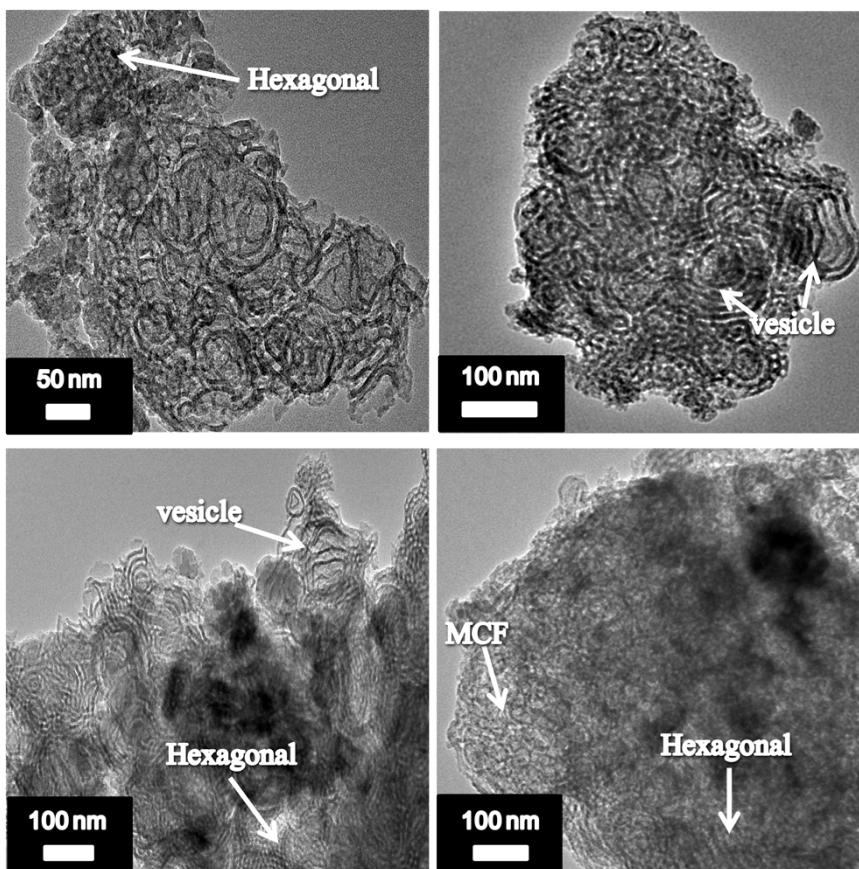
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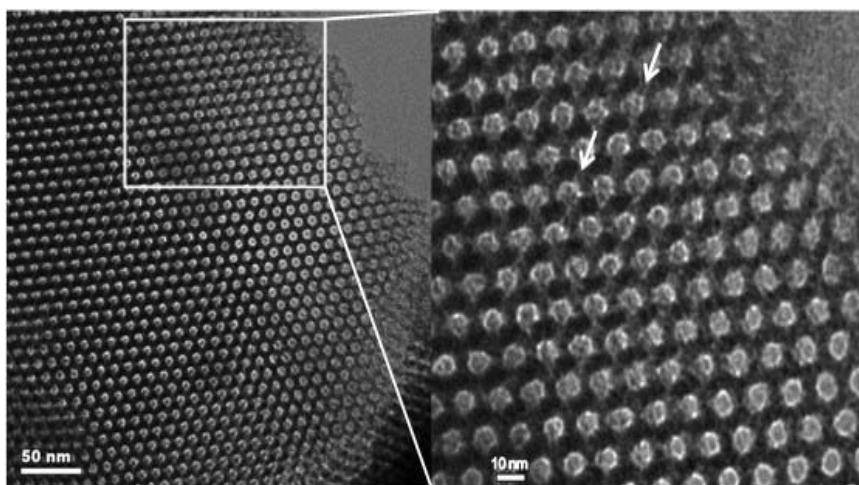
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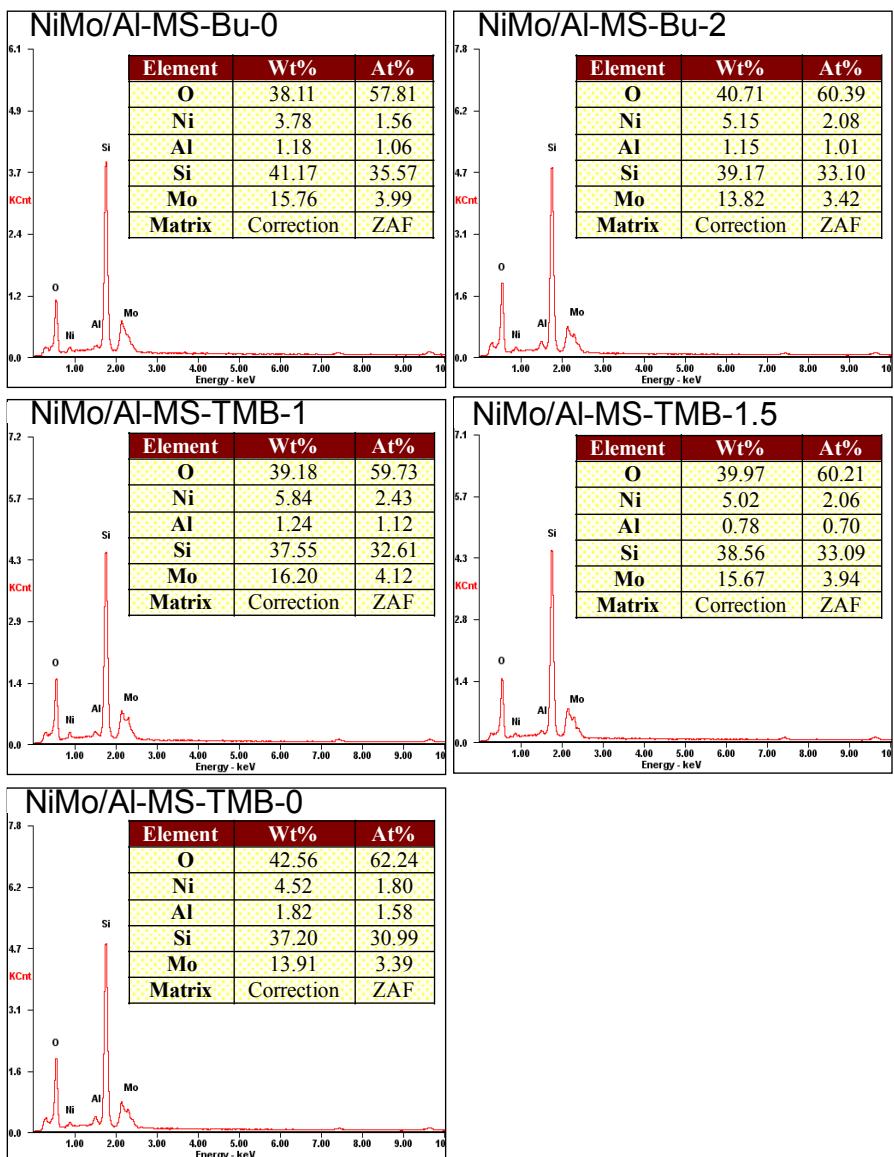
**Figure S1.** SEM images of calcined mesostructured silicas synthesized with different Bu/TMB molar ratios. a) MS-Bu-0, b) MS-Bu-0.5, c) MS-Bu-1, d) MS-Bu-2, e) MS-Bu-3, f) MS-Bu-4.



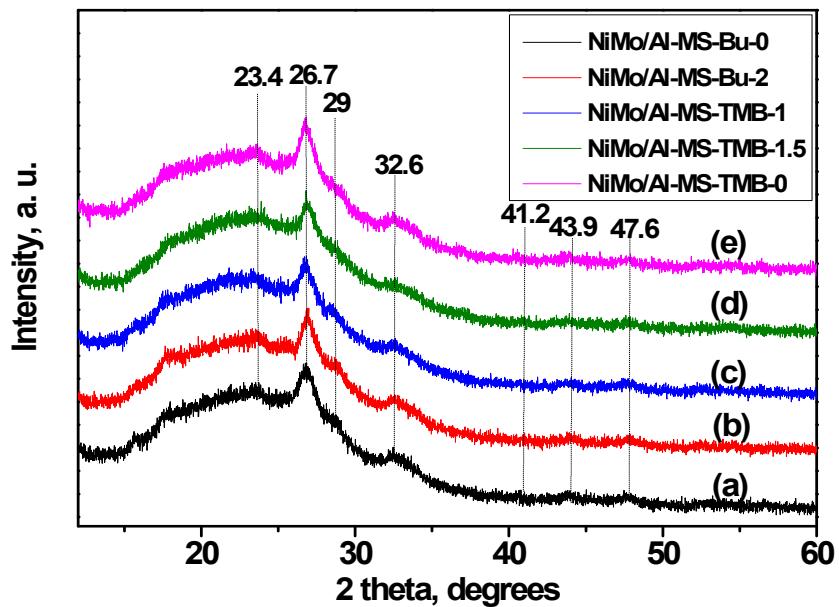
**Figure S2.** Representative TEM images of MS-TMB-1 calcined sample synthesized with the molar ratio TMB/Bu=1.



**Figure S3.** TEM images of the calcined sample MS-TMB-0 with the molar ratio TMB/Bu=0.



**Figure S4.** SEM-EDS elemental analysis results of all the prepared NiMo/Al-MS catalysts.



**Figure S5.** High angle XRD patterns of all the prepared NiMo/Al-MS catalysts. (a) NiMo/Al-MS-Bu-0, (b) NiMo/Al-MS-Bu-2, (c) NiMo/Al-MS-TMB-1, (d) NiMo/Al-MS-TMB-1.5, (e) NiMo/Al-MS-TMB-0.

**Table S1. Texture parameters of the hierarchically porous silicas synthesized with different Bu/TMB molar ratios**

Sample	Structure <sup>a</sup>	d spacing [nm] <sup>b</sup>	BET surface area [m <sup>2</sup> ·g <sup>-1</sup> ]	Total Pore Volume [cm <sup>3</sup> ·g <sup>-1</sup> ]	t-plot [cm <sup>3</sup> ·g <sup>-1</sup> ]	Pore diameter [nm] <sup>c</sup>
MS-Bu-0	MCF	-	624	0.91	0.14	11.5
MS-Bu-0.5	Hex+Ves	-	812	1.11	0.19	5.6, 7.7
MS-Bu-1	Hex+Ves	-	622	0.88	0.15	8.0
MS-Bu-2	Ves	-	481	1.34	0.084	5.6, 17.9
MS-Bu-3	Hex	10.9	747	0.87	0.21	8.8
MS-Bu-4	Hex	10.6	693	0.73	0.21	7.8

<sup>a</sup> For the structure of materials, “Hex” represents “hexagonal”, “Ves” denotes “vesicle” and “MCF” stands for “mesocellular foam”.  
<sup>b</sup> The d-spacing values were calculated from the prime peak in Figure 1.  
<sup>c</sup> Determined from the adsorption branch on the basis of BJH model.

**Table S2. Texture parameters of the hierarchically porous silicas synthesized with different TMB/Bu molar ratios**

Sample	Structure <sup>a</sup>	d spacing [nm] <sup>b</sup>	BET surface area [m <sup>2</sup> ·g <sup>-1</sup> ]	Total Pore Volume [cm <sup>3</sup> ·g <sup>-1</sup> ]	t-plot [cm <sup>3</sup> ·g <sup>-1</sup> ]	Pore diameter [nm] <sup>c</sup>
MS-TMB-0	Hex	10.3	805	1.04	0.14	9.6
MS-TMB-0.12	Hex	10.5	654	0.97	0.17	9.8
MS-TMB-0.24	Hex	10.7	708	0.96	0.13	9.9
MS-TMB-0.38	Hex	10.8	719	0.94	0.16	10.0
MS-TMB-1	Hex+Ves+MCF	-	665	1.13	0.18	7.7, 12.6
MS-TMB-1.5	SBA+MCF	-	694	1.20	0.14	9.8, 13.2
MS-TMB-2	SBA+MCF	-	640	1.21	0.13	12.5, 17.9

<sup>a</sup> For the structure of materials, “Hex” represents “hexagonal”, “Ves” denotes “vesicle”, “SBA” in the name of “disordered-SBA-15-type” “MCF” stands for “mesocellular foam”.  
<sup>b</sup> The d-spacing values were calculated from the prime peak in Figure 4.  
<sup>c</sup> Determined from the adsorption branch on the basis of BJH model.

**Table S3. The analysis results of Si/Al molar ratio by ICP-OES for the Al-MS materials**

Sample	Structure <sup>a</sup>	Si/Al molar ratio
Al-MS-Bu-0 (Si/Al=20)	MCF	24.4
Al-MS-Bu-2 (Si/Al=20)	Ves	25.4
Al-MS-TMB-1 (Si/Al=20)	Hex+Ves+MCF	24.0
Al-MS-TMB-1.5 (Si/Al=20)	SBA+MCF	25.6
Al-MS-TMB-0 (Si/Al=20)	Hex	24.8

<sup>a</sup> For the structure of materials, “Hex” represents “hexagonal”, “Ves” denotes “vesicle”, “SBA” in the name of “disordered-SBA-15-type” “MCF” stands for “mesocellular foam”.