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Dispersion of Mo in mesoporous molybdosilicates

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Introduction

The substitution of Si in mesoporous silicas by another elements has attracted considerable attention. Although many of them have been carried out in usual hydrothermal syntheses, some catalytically important metal ions are precipitated in alkaline conditions. We have achieved high Mo loading by incorporating ammonium heptamolybdate (AHM) into SBA-1 and SBA-3, mesoporous silicas prepared in acidic solutions. Mo oxides in a supported Mo catalyst have usually structural variations, which reduce the coordination numbers. That of Mo-Mo bond is a measure of the dispersion of Mo and those of Mo-O bonds reflects the uniformity of the structure. We have compared these parameters from EXAFS analyses among Mo-SBA-1, Mo/SBA-1, Mo-SBA-3 and Mo/SBA-3.

Experimental

Two kinds of mesoporous silicas, SBA-1 and SBA-3, have different structure, cubic (*Pm3n*) and hexagonal (*p6m*), respectively. Mo-SBA-1 (Mo-SBA-3) was synthesised by preparing SBA-1 (SBA-3) in the presence of AHM in acidic condition. Mo/SBA-1 (Mo/SBA-3) was prepared by an incipient wetness method of calcined SBA-1 (SBA-3) with aqueous AHM solution. All catalysts were oxidized at 673 K before the measurement of XAFS spectra at BL-10B. Data analysis was carried out through REX 2000 and WinXAS 2.1. For an oxygen scatterer, the backscattering amplitude and the phase shift were extracted from EXAFS of Na_2MoO_4.

Results and Discussion

The parameters obtained by the analysis of EXAFS spectra are listed in Table 1. Two Mo-O bonds were distinguished whose coordination numbers were smaller than expected from Mo (VI) oxides. This is caused by the overlay of various oscillations having similar but different phase shifts. The longer bond around 0.2 nm is assigned to Mo-O and the shorter one around 0.16 nm is to Mo=O. The parameters on Mo-O do not depend on the loading of Mo. *N*(Mo-Mo) appears more than 3 wt % and the difference among the catalysts is observed. It is in the order of Mo-SBA-1>Mo/SBA-1~Mo-SBA-3>Mo-SBA-3. It is likely that the coordination number increases with the agglomeration of MoOx and, consequently, the dispersion is in the inverse order.

The transition appeared at the preedge region, which is considered as a 1s-4d transition of T_d MoO_4. Its integrated absorbance slightly increased according to Mo dispersions.

Table 1. Structural parameters of Mo-SBA-1, Mo/SBA-1, Mo-SBA-3, and Mo/SBA-3.

		Mo-O			Mo-Mo	
Mo/%	*N*	*r* /nm	*Dw*	*N*	*r* /nm	*Dw*
		Mo-	**SBA-1**			
1.07	1.5	0.169	0.027			
	1.1	0.207	0.045			
1.71	1.4	0.164	0.049			
	1.0	0.214	0.068			
3.36	1.2	0.164	0.049	0.59	0.324	0.091
	1.0	0.209	0.047			
9.45	1.3	0.163	0.045	0.65	0.326	0.090
	1.1	0.209	0.059			
		Mo/	**SBA-1**			
2.91	1.4	0.169	0.035			
	1.1	0.203	0.060			
3.79	1.2	0.169	0.055	0.32	0.326	0.067
	1.0	0.201	0.066			
		Mo-	**SBA-3**			
2.26	1.4	0.170	0.047			
	1.0	0.228	0.086			
3.91	1.3	0.171	0.076	0.31	0.327	0.064
	1.0	0.216	0.088			
		Mo/	**SBA-3**			
2.26	1.4	0.160	0.035			
	1.2	0.211	0.075			
3.91	1.2	0.165	0.090	0.21	0.319	0.066
	1.0	0.210	0.090			

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