

Hydration of Mo species in Mo dispersed in SBA-1

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Introduction

The working of active atoms during heterogeneous catalytic reactions has been a topic on the supported Mo catalysts. The size of the ensembles depends on the preparation procedure. Direct incorporations of Mo into the framework of mesoporous silica are a technique newly developed. SBA-1 is synthesized in acid conditions, which is favorable to incorporate significant amount of Mo into the silica pores. We study the dispersion of Mo in hydrated and dehydrated states by EXAFS spectroscopy.

Method

Mo-SBA-1 was prepared as follows. An aqueous solution of hexaammonium heptamolybdate (AHM) and tetraethyl orthosilicate (TEOS) was added to an aqueous solution of CTEABr acidified with HCl with stirring vigorously at 273 K. The mixture was kept at 273 K for 4 d. Yellow precipitates were filtered, dried and calcined. The Mo content in Mo-SBA-1 was determined by ICP. Mo/SBA-1 was prepared by impregnating respective mesoporous silicas with an aqueous solution of AHM acidified with HCl, dried, and calcined.

Samples for spectroscopic measurements were pretreated by heating at 673 K in oxygen and evacuation at room temperature. These dehydrated catalysts were transferred into suitable spectroscopic cells without exposure to air. Hydration treatments were conducted in the atmospheric environment, i.e. at 298 K and 50-70 % of humidity. X-ray absorption experiments were carried out in a transmission mode at BL-10B. The data were processed by EXAFS analysis program REX 2000 (Rigaku). k^3 -Weighted EXAFS oscillation, $k^3\chi(k)$, in the 35 – 135 nm⁻¹ region was Fourier transformed to a radial distribution function. Peak due to Mo-Mo bonds were separately inverse Fourier transformed into k space where the curve fitting analyses were done. The amplitude and phase-shift functions for Mo-Mo were extracted from the spectra of Mo foil.

Results and Discussion

Table 1 shows the coordination number of Mo nearest neighbour in Mo K-edge EXAFS. Comparing under the same preparing conditions, the coordination number is larger in the direct incorporation catalyst than in the impregnation one. For example, dehydrated 6.25 wt % Mo-SBA-1 and Mo/SBA-1 show $N(\text{Mo-Mo}) = 0.7$ and

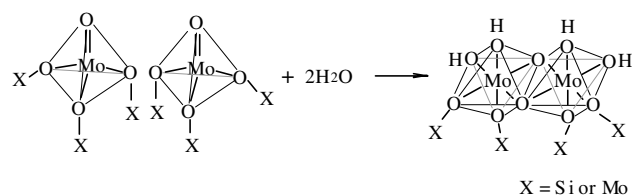
0.4, respectively. Hydration increases not only $r(\text{Mo-Mo})$ but also $N(\text{Mo-Mo})$ and the degree of the enhancement is larger in the direct incorporation catalyst than in the impregnation one. Mo-Mo bond was not detected in the radial distribution function for dehydrated 1.69 wt % Mo-SBA-1, while it clearly appeared after hydration.

Table 1. Curve fitting results of Mo K-edge EXAFS of Molybdsilicates

condition	catalyst	wt%	N	Mo-Mo	
				r/nm	Dw
dehydrated	Mo-SBA-1	1.06	(0)		
		1.69	(0)		
		3.85	0.6 ³	0.324	0.091
		6.25	0.7 ³	0.326	0.090
dehydrated	Mo/SBA-1	2.95	(0)		
		6.25	0.4 ²	0.327	0.071
hydrated	Mo-SBA-1	1.06	(0)		
		1.69	0.6 ²	0.330	0.066
		3.85	1.1 ⁴	0.331	0.064
		6.25	1.4 ⁴	0.331	0.075
hydrated	Mo/SBA-1	2.95	(0)		
		6.25	0.5 ²	0.331	0.067

N : coordination number, r : interatomic distance and Dw : relative Debye-Waller factor against that of the reference samples ($Dw_{\text{ref}} = 0.06$). The superscripts of the data are estimated errors. That for $r(\text{Mo-Mo})$ is 0.003 nm.

Hydration likely results in a bridging reaction of MoO_x units on the pore surface such as



Especially for Mo-SBA-1, the ensemble of MoO_x units remains even without the chemical bond, which implies the possibility of the activation of a molecule by more than two MoO_x units working in a corporation. The lower dispersion by the direct incorporation is likely caused by a partial inclusion AHM molecular ion in the pore wall during hydrothermal synthesis while it is just adsorbed on the pore wall during impregnation.

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