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Analysis of local structure of nickel ions in Ni-MCM-41 having different pore size

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Introduction

Nickel ions-supported mesoporous silica MCM-41 (Ni-MCM-41) exhibits high levels of catalytic activity in the ethene dimerization reaction, as well as for the selective conversion of ethene to propene by controlling the reaction condition[1]. Recently, we found that the catalytic activity for ethene dimerization significantly changes depending on the pore size of Ni-MCM-41 (pore diameter: 2.0, 2.9, and 3.9 nm). That is, the Ni-MCM-41 sample with the lowest pore size (2.0 nm), which had been evacuated at 673 K, was most active for the reaction, and the activity declined as the pore size of Ni-MCM-41 increases. The difference has been rarely observed in the state of major part of nickel ions on Ni-MCM-41 having different pore size. From the measurements of the diffuse reflectance UV-Vis and the IR spectra using nitrogen monoxide as a probe molecule, however, it has found that the coordinatively unsaturated Ni^{2+} ions, 3-coordinated Ni^{2+} ions, are easily formed in Ni-MCM-41 having smaller pore size by the evacuation at 673 K. The possibility that the 3-coordinated Ni^{2+} ions act as the active site for ethene dimerization is the highest. However, it is not clear why the unsaturated Ni^{2+} ions are easily formed in Ni-MCM-41 with smaller pore size. In this study, for the Ni-MCM-41 samples having different pore size, the analysis of the local structure of nickel ions in Ni-MCM-41 was performed by utilizing the X-ray absorption fine structure spectroscopy. The nickel ions were supported by using the template-ion-exchange method[2]. The nickel loading was adjusted to initial Si/Ni ratio of 20. The used samples are as follows; Ni-MCM-41-A (pore diameter: 2.0 nm), Ni-MCM-41-B (2.9 nm), and Ni-MCM-41-C (3.9 nm).

Results and Discussion

For each Ni-MCM-41 sample, two bands were observed at around 0.16 and 0.27 nm (no phase-shift correction) after evacuation at 673 K. The former band is assigned to back-scattering from the nearest neighboring oxygen atoms, and the latter one back-scattering from the nearest neighboring silicon and/or nickel atoms[3]. The parameters, which were obtained by analysis of the EXAFS data using the least-square method for the 673 K-treated Ni-MCM-41 samples, are summarized in Table 1. For all samples, the coordination number of the first shell is nearly equal to the value of the poor crystallized nickel phyllosilicate having layered structure reported by Carriat et al.[3]. Here, it is considered that the coordination number of silicon atoms for each sample provides the useful information on the state of MCM-41 pore surface. For Ni-MCM-41-A and Ni-MCM-41-B, the value is approximately 3. For Ni-MCM-41-C, the one is 3.5. We observed the IR band at around 570 cm^{-1} due to five-membered rings consisting of Si–O for all the Ni-MCM-41 samples[4,5]. Generally, the framework of amorphous silica consists of six-membered rings. The coordination number of silicon atoms obtained for each sample can be explained by the consideration of the presence of five- and six-membered rings in Ni-MCM-41. The pore of MCM-41 bears a curvature depending on the pore size. Therefore, the five- and six-membered rings composing MCM-41 pore surface curve to the interior side in the rings, which take the boat-type structure. When the five-membered ring bends inside, the number of silicon atoms which are adjacent to nickel ion supported on such a ring becomes 3. Similarly, the number of silicon atoms on six-membered ring is 4. Considering mentioned above, nickel ions in Ni-MCM-41-A and Ni-MCM-41-B locate on five-membered rings, and the ones in Ni-MCM-41-C on five- and six-membered rings. It has been already found that the coordinatively unsaturated nickel ions, 3-coordinated Ni^{2+} ions, are formed in the Ni-MCM-41 sample with smaller pore size. Namely, it is thought in a similar manner as above that 3-coodinated Ni^{2+} ion is formed in five-membered ring. In the case of six-membered ring, 4-coodinated Ni^{2+} ion is anticipated to be formed. From these results, it was found that the five-membered rings are easily formed in MCM-41 having smaller pore size and that the five-membered rings bring the nickel ions into the favorable position to stable formation of 3-coordinated state.

Table 1: Fitted structure parameters of the respective samples

Ni-MCM-41-A			Ni-MCM-41-B			Ni-MCM-41-C		
neighbors	*N*	*R* (nm)	neighbors	*N*	*R* (nm)	neighbors	*N*	*R* (nm)
O	5.9	0.206	O	6.0	0.206	O	6.3	0.206
Si	2.7	0.328	Si	2.8	0.328	Si	3.5	0.327
Ni	2.9	0.304	Ni	3.7	0.303	Ni	3.5	0.303

N: Coordination number, *R*: Interatomic distance.

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