

XAFS study of local structure of nickel ions in Ni-MCM-41 prepared by different methods

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Introduction

Recently, nickel ions-supported MCM-41 (Ni-MCM-41) has been found to exhibit high levels of catalytic activity on the selective conversion of ethene to propene and butenes[1]. Although the importance of supported nickel ions and of the pore structure of MCM-41 has been suggested, the state of nickel ions in MCM-41 is not completely clarified. In this study, for two kinds of Ni-MCM-41 materials prepared by using the template ion-exchange and the direct hydrothermal methods (denoted as Ni(TIE)-MCM-41 and Ni(DH)-MCM-41, respectively), the analysis of the local structure of nickel ions in Ni-MCM-41 was performed by utilizing the X-ray absorption fine structure spectroscopy.

Results and discussion

The EXAFS spectra for the Ni(TIE)-MCM-41 and Ni(DH)-MCM-41 samples evacuated at different temperatures from 300 K to 873 K are shown in Figure 1. For both samples, two peaks were observed at around 1.6 and 2.7 Å (no phase-shift correction). The former peak is assigned to back-scattering from the nearest neighboring oxygen atoms, and the latter one to back-scattering from the nearest neighboring silicon and/or nickel atoms. By comparing the spectra for both samples evacuated at each temperature, it is clear that the ratio of the intensity of the first to the second band is largely different in the magnitude, suggesting that in both samples the local structure of nickel ions is different. The parameters, which were obtained by analysis of the EXAFS data using the least-square method, are summarized in Table 1. For 300 K-treated Ni(TIE)-MCM-41, the coordination numbers obtained for the first and second coordination shells are nearly equal to the data reported by Carriat et al. for the poor crystallized nickel phyllosilicate having layered structure[2]. The Ni(TIE)-MCM-41 sample showed the characteristic IR bands at 3628, 710, and 670 cm^{-1} due to 2:1 nickel phyllosilicate which consists of brucite-type sheets sandwiched by two sheets of SiO_4 units[2]. Moreover, the diffuse reflectance (DR) UV-Vis spectrum presented only the d-d transition bands due to Ni^{2+} ions in the octahedral configuration. These facts indicate that Ni^{2+} ions in Ni(TIE)-MCM-41 interact with MCM-41 surface to form 2:1 nickel phyllosilicate along the pore wall. Since the value of $N_{\text{Ni-O}}$ for 873 K-treated sample is about six ($N_{\text{Ni-O}}=5.9$), it was found that the 2:1 nickel phyllosilicate species with octahedral configuration still retain at 873 K. The coordination numbers of the first and second shells for Ni(DH)-MCM-41 are smaller than those for Ni(TIE)-MCM-41. For 300 K-treated Ni(DH)-

MCM-41, the value of $N_{\text{Ni-O}}$ was evaluated to be 4.7, and the d-d transition bands due to Ni^{2+} ions in both the octahedral and distorted tetrahedral configurations were observed; it was suggested the existence of Ni^{2+} ions which were not coordinated by water molecules. Furthermore, the IR bands at 3621 and 670 cm^{-1} appeared. These bands can be attributable to bands of nickel silicate located in MCM-41 surface. On the basis of the data of DR UV-Vis spectrum, only the octahedral (6-coordinated) and distorted tetrahedral (4-coordinated) nickel ions are presented in Ni(DH)-MCM-41. By assuming that the total number of nickel ions, n_{total} , is unity and using the value of $N_{\text{Ni-O}}$ (4.7), the ratio of the number of 6-coordinated and 4-coordinated nickel ions to the total number of nickel ions, n_6/n_{total} and n_4/n_{total} , respectively, were estimated to be 0.35 and 0.65, respectively. From these results, it was evaluated that 35% of nickel species, which have octahedral configuration, are presented in the vicinity of MCM-41 surface, and the residual species (65%) take the distorted tetrahedral configuration. These species seem to be incorporated into MCM-41 pore wall. Moreover, the former species was found to transform into 4-coordinated nickel species after the evacuation at 873 K since the value of $N_{\text{Ni-O}}$ is four.

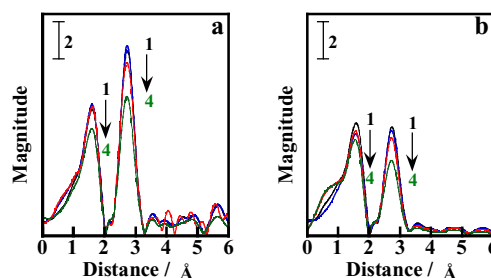


Figure 1: EXAFS spectra for (a) Ni(TIE)-MCM-41 and (b) Ni(DH)-MCM-41; (1) 300 K, (2) 473 K, (3) 673 K, and (4) 873 K.

Table 1: Fitted structure parameters of the respective samples

Ni(TIE)-MCM-41				Ni(DH)-MCM-41			
	neighbors	N	R (Å)		neighbors	N	R (Å)
300 K	O	6.8	2.07	300 K	O	4.7	2.05
	Si	3.0	3.28		Si	2.6	3.27
	Ni	4.2	3.04		Ni	3.6	3.06
873 K	O	5.9	2.06	873 K	O	4.0	2.03
	Si	2.7	3.27		Si	2.2	3.25
	Ni	3.1	3.02		Ni	2.3	3.03

N : Coordination number, R : Interatomic distance.

References

- [1] M. Iwamoto and Y. Kosugi., J. Phys. Chem. C 111, 13 (2007).
 - [2] J. Y. Carriat et al. J. Am. Chem. Soc. 120, 2059 (1998).
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