Size Regulation of Supported Ni Nanocluster Catalyst by Using Alcoholate as Bifunctional Reagent

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1 Introduction

Great attention has been paid to the metal nanocluster due to the both scientific interests and the potential applications in industrial fields. Ni element is one of the most useful catalyst materials since it is active for many reactions as well as abundant. Development of the catalysis will be expected by reducing the Ni particle size down to nanocluster since nanocluster has a larger population of low-coordination sites and may have a specific property. However, conventional preparation methods of supported Ni catalysts may give the metal particle size larger than 10 nm, and hence, the development of the size regulated Ni nanocluster preparation is expected.

In this study, we demonstrate the preparation and control the size of supported Ni nanocluster catalyst by changing alkyl chain length of alcoholate. The cluster size of Ni was determined XAFS analysis.

2 Experimental

Alcoholate stabilized Ni colloid was prepared as in the literature [1]; in this study, five different alcohols were applied as alcoholate precursors; 2-propanol (C3), 2-butanol (C4), 2-pentanol (C5), 2-octanol (C8) and 2-decanol (C10). The obtained Ni colloid was impregnated into Al_2O_3 powder (Aerosil, alumina-C) and stirred for 3 h, followed by solvent removal, washing with distilled water and drying *in vacuo* overnight. The Ni loadings were regulated to 3 wt%.

Ni *K*-edge EXAFS were collected at PF BL-9C with Si(111) double crystal monochromator in a transmission mode. Curve-fitting analysis of k^3 -weighted EXAFS oscillations in *k*-space were performed by the program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis were extracted from bulk Ni metal.

3 Results and Discussion

FT of Ni K-edge EXAFS oscillations (k^3 -weighted) are shown in Fig. 1. Coordination number (CN) for Ni-Ni coordination at around 0.21 nm were calculated by use of model parameters. The CN decreased with the lengthening alkyl chain length from C3 (CN=8.5) to C8(CN=7.3). However, lengthening of alkyl chain length longer than C8, the CN became large as 10.3 (C10). Alcoholate has two competing function, one is reducing agent of the Ni(II) ion to Ni(0) and the other is stabilizing agent of the resulting Ni(0) clusters. The reducing ability was quantitatively estimated by the color-change time during the preparation process (from green to black), and determined as following oreder; C3 > C4 > C5 > C8 > C10. On the other hand, in terms of stabilizing effect, alcoholate with long alkyl chain length can prevent the cluster from the aggregation. On the basis of the above consideration, the formation of the smallest Ni nanoclusters by use of C8 can be explained between these two competing effects [2].



Fig. 1. FT of k^3 -weighted Ni *K*-edge EXAFS for supported Ni catalysts and reference compounds; (a) *col* Ni/Al₂O₃(*C3*), (b) *col* Ni/Al₂O₃(*C4*), (c) *col* Ni/Al₂O₃(*C5*), (d) *col* Ni/Al₂O₃(*C8*), (e) *col* Ni/Al₂O₃(*C10*), (f) Ni foil.

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