

Promoting effect of the interfacial Ni-O-Si structure on silica supported NiO nanocluster catalyst for the 1-phenylethanol oxidation reaction

Takuro SASAKI, Nobuyuki ICHIKUNI*, Takayoshi HARA and Shogo SHIMAZU
Chiba University, Inage-ku, Chiba 263-8522, Japan

1 Introduction

Support itself has some important roles on the solid catalysis; maintaining the high surface area, stabilizing the dispersion of active species during the catalysis. Furthermore, the support can produce a synergy effect with active species and promote catalytic reactions [1].

In this work, we tried to develop supported NiO nanocluster catalysts and to reveal its interfacial structure by utilizing XAFS. As a consequence, promoting effect of the interfacial structure between NiO nanocluster and SiO₂ for 1-phenylethanol oxidation reaction was found.

2 Experimental

SiO₂ (Fuji Silysia Chemical Ltd., CARIAC P-10) or activated carbon (Wako Pure Chemical Industries Ltd.) supported NiO catalysts were prepared by an impregnation method. NiO(amm)/SiO₂-*T* and NiO(amm)/AC, NiO(ace)/SiO₂-*T* and NiO(nit)/SiO₂-*T* were obtained by using [Ni(NH₃)₆](NO₃)₂, Ni(acac)₂ and Ni(NO₃)₂ as a precursor, respectively, followed by heat treatment at *T* (K) in air. The heat treatment temperature was altered as RT, 573, 673 and 773 K. Ni loading amount was regulated to 5 wt%. Ni *K*-edge XAFS data were obtained at PF BL-9C (Proposal No.: 2016G069) of IMSS-KEK by using Si(111) double crystal monochromator in a transmission mode at room temperature.

3 Results and Discussion

Figure shows Ni *K*-edge XANES of NiO catalysts and reference compounds. XANES shape of all catalysts (Fig. c-h) was similar to that of bulk NiO (Fig. a). Additionally, NiO(amm)/SiO₂-RT, -573 and -773 (Fig. f-h) showed two shoulders at 8346 eV (peak α) and 8350 eV (peak γ) besides peak β (at 8349 eV). Those two peaks were characteristic of nickel silicate as shown in Fig. b. This result indicates that NiO and Ni-O-Si structure coexisted on NiO(amm)/SiO₂-*T* catalysts. The ratio of Ni-O-Si structure was lowered as increasing the treatment temperature (Table 1).

Moreover, XAFS measurements revealed that the particle size of NiO can be controlled by changing the Ni precursor, support and treatment temperature as shown in Table 1.

NiO nanocluster on the interfacial Ni-O-Si structure showed higher activity than NiO nanocluster only did, which indicated that Ni-O-Si structure had the promoting effect for this reaction and that effective contribution of interfacial Ni-O-Si structure was a key factor for this reaction.

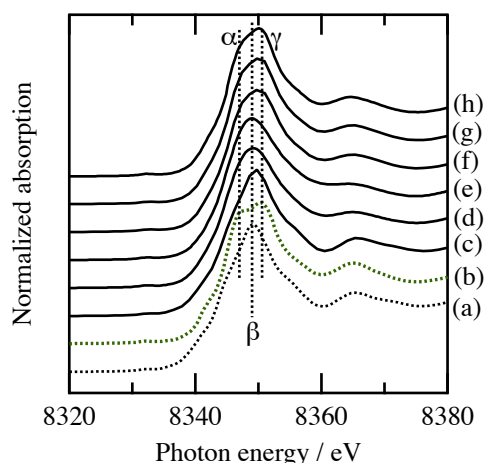


Fig. Ni *K*-edge XANES spectra of NiO catalysts (c-h) and reference compounds (a, b): (a) bulk NiO, (b) bulk nickel silicate^a, (c) NiO(nit)/SiO₂-673, (d) NiO(ace)/SiO₂-673, (e) NiO(amm)/AC-573, (f) NiO(amm)/SiO₂-773, (g) NiO(amm)/SiO₂-573, (h) NiO(amm)/SiO₂-RT. ^aPrepared by a method reported in [2].

Table 1 Coordination number of Ni-Ni, ratio of Ni-O-Si structure and yield of 1-phenylethanol oxidation^a

Catalyst	CN ^b	Ni-O-Si ratio ^c (%)	Yield ^d (%)
NiO(amm)/SiO ₂ -RT	7.3	63	51
NiO(amm)/SiO ₂ -573	7.4	52	28
NiO(amm)/SiO ₂ -773	8.0	43	4.5
NiO(amm)/AC-573	5.0	0	17
NiO(ace)/SiO ₂ -673	7.0	0	7.8
NiO(nit)/SiO ₂ -673	12	0	1.9

^a1-Phenylethanol (1 mmol), NiO catalyst (0.10 g, S/C = 12), solvent: *p*-xylene (5 mL), atmosphere: O₂ (1 atm), reaction temperature: 373 K, reaction time: 6 h. ^bCoordination number of the nearest Ni-Ni coordination. ^cDetermined by XANES pattern fitting analysis. ^dDetermined by gas chromatography using an internal standard technique.

Acknowledgement

This study was supported by JSPS KAKENHI Grant Number 23560928 and 26420784.

References

- [1] T. Sasaki *et al.*, *Catal. Today* **307**, 29 (2018).
[2] M.V. Sivaiah *et al.*, *Micro. Meso. Mater.*, **140**, 69 (2011).

* ichikuni@faculty.chiba-u.jp