Catalysis Letters 20 (1993) 117–124

Asymmetric structure analysis of active surface-sites by in situ polarized total-reflection fluorescence EXAFS

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An in situ polarization-dependent total reflection fluorescence yield EXAFS system has been developed to analyze the asymmetric structures of catalytically active metal sites on single crystal surfaces. This technique separately reveals the bonding feature parallel and perpendicular to the support surface. The systems of Cu ion on α-quartz(0001), Co oxide on α-alumina(0001), and Pt_4 on α-alumina(0001) were investigated as model surfaces of supported catalytic systems. The location of Cu sites on α-quartz(0001), the epitaxial growth mode of Co_3O_4 on α-alumina(0001), and the Pt raft structure with metal–support interaction in Pt_4/α-alumina(0001) were observed.

Keywords: Polarized total reflection EXAFS; EXAFS of Cu on α-quartz; EXAFS of cobalt oxide on α-alumina; EXAFS of platinum on α-alumina

1. Introduction

Conventional catalysts are often used in supported catalysts where active metal sites are dispersed on inorganic oxides. EXAFS (extended X-ray absorption fine structure) is a powerful tool for the structure analysis of active sites on inorganic oxide supports. Conventional EXAFS experiments are carried out for high surface area powder catalysts in a transmission mode, but it gives averaged information on the local structure around the active sites. However, the structures of active sites on surfaces are not naturally symmetric; the structure parallel to the surface may be different from that perpendicular to the surface. Moreover, active sites during reactions may dynamically change in lateral and vertical directions. For example, Mo sites of the Mo dimer catalysts during C_2H_5OH oxidation dynamically change by 0.4 Å laterally and by 0.1 Å vertically [1]. Thus it is important to determine the asymmetric structure change of active sites under in situ conditions in order to understand reaction mechanisms and essential factors for catalysis which will lead to the development of new catalytic materials.

K-edge EXAFS oscillation $\chi(k)$ has a polarization dependency as

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$$\chi(k)=\frac{F(k)\exp(-2\sigma^2k^2)\sin[2kr+\phi(k)]}{kr^2}\sum_j^N 3\cos^2\theta_j, \tag{1}$$

where $F(k)$ and $\phi(k)$ are backscattering amplitude and phase shift functions, respectively. The σ, k, r, and N are Debye–Waller factor, wave number of photoelectron, bond length, and coordination number, respectively. θ_j is the angle between the electric-field vector and bond direction as shown in fig. 1.

If a single crystal is used as support instead of powder, the polarization-dependent EXAFS can give information on the bonding parallel and perpendicular to the support surface, separately. When the electric-field vector is parallel to the surface ($E \parallel S$), the atomic arrangement in a lateral direction can be determined. On the other hand, when it is perpendicular to the surface ($E \perp S$), one can get information about atomic arrangement in a vertical direction.

Single crystal samples, however, have a low surface area and the number of active sites on single crystal surface is small. Thus the fluorescence detection with high S/B (signal to background ratio) is useful for this sort of sample [2]. In the hard X-ray regions where many catalytically interesting elements (Cu, Fe, Co, Pt, etc.) absorb, the scattering from substrate bulk is too large to observe EXAFS signals with high S/B emitted from active sites on surfaces even by the fluorescence detection mode. Heald et al. showed that the strong scattering from bulk can be reduced to negligible level when X-ray light hits the sample with less than a critical angle of total reflection [3].

Thus by a combination of total-reflection fluorescence method and polarization-dependent EXAFS technique, one can get information about the asymmetric structure of active sites on single crystal surfaces which are regarded as model catalyst surfaces.

In this paper we will briefly report the in situ chamber for polarization-dependent total-reflection fluorescence-yield EXAFS measurements and the asymmetric structure determination of active sites on single crystals.

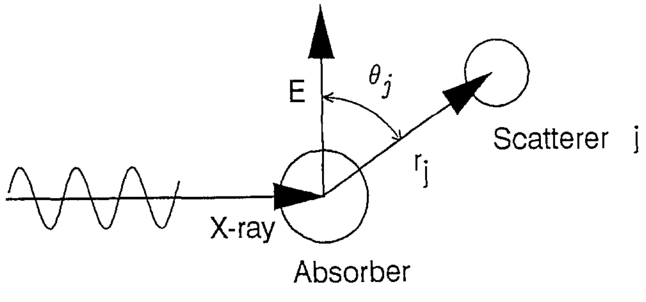

Fig. 1. Relation between electric-field vector(E) and bond direction (r).

2. Experimental

2.1. IN SITU EXAFS CHAMBER

Fig. 2 shows the in situ chamber for polarization-dependent total-reflection fluorescence yield EXAFS measurements. The details of this chamber will be described elsewhere [4], but the chamber system is briefly summarized here. The chamber is composed of an upper part and a lower part. The model sample is prepared in the upper preparation chamber by CVD (chemical vapor deposition), vacuum evaporation method or so on. The upper chamber can be isolated from the lower chamber by a gatevalve to prevent the X-ray windows from being contaminated by metal vapor during sample preparation. Fluorescence emitted from the sample is detected through the side window by a scintillation counter. There are a rotary table and three mini-jacks under the EXAFS chamber, which are used to adjust the total-reflection conditions. The sample can also be rotated with the sample holder along the X-ray beam direction as shown in fig. 3. The system makes it possible to set the sample at the total reflection conditions in both $E \parallel S$ and $E \perp S$ orientations successively under in situ conditions without breaking the vacuum of the system.

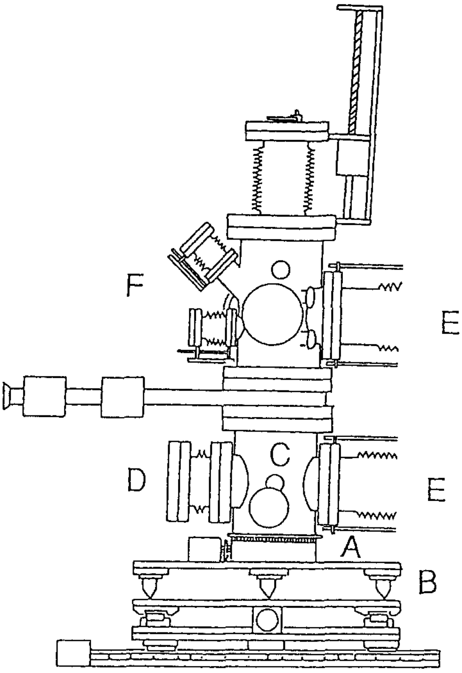

Fig. 2. In situ EXAFS apparatus. A: rotary table; B: mini-jack; C: X-ray window; D: window for X-ray fluorescence; E: to vacuum; F: preparation chamber.

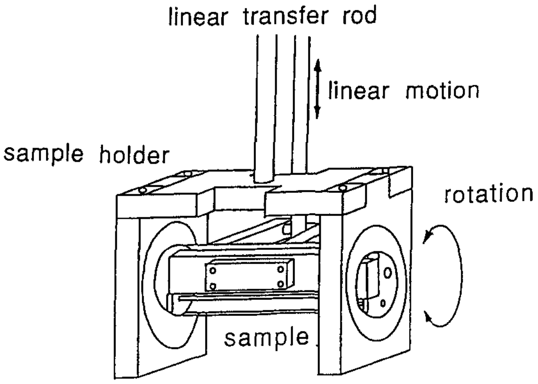

Fig. 3. Sample holder. The linear transfer rod behind the sample rotates the sample around the X-ray beam direction, to get $E \parallel S$ and $E \perp S$.

2.2. EXAFS MEASUREMENTS

EXAFS measurements were carried out at BL14A and BL7C of Photon Factory (K PF), using a double crystal Si(111) monochromator (Proposal No. 85-011, No. 89-146, 90-142). For Co and Cu, a total-reflection mirror was used to remove the higher harmonics. The incident X-ray was monitored by an ionization chamber and the fluorescent X-ray was monitored by a scintillation counter. The data were analyzed by a curve fitting method. Reference compounds used for the analysis of Co and Cu samples were Co_3O_4 and CuO, respectively.

3. Results and discussion

3.1. Cu ION ON α-QUARTZ(0001)

In order to check the ability of the polarization-dependent total-reflection fluorescence yield EXAFS method, we first studied Cu ion on α-quartz(0001) derived from $Cu(DPM)_2$ (DPM: dipyvaloylmethanate) [5]. $Cu(DPM)_2$ has been reported to stoichiometrically react with two OH groups of SiO_2 powder [6]. The α-quartz(0001) was pretreated at 393 K for 2 h and was interacted with $Cu(DPM)_2$ vapor, followed by thermal treatment at 673 K for 2 h in air. The ratio of Cu atom to surface oxygen atoms on α-quartz(0001) was estimated to be 0.4 ± 0.2 by an ICP analysis. The EXAFS Fourier transforms for Cu/SiO_2 with $E \parallel S$ and $E \perp S$ showed one peak corresponding to Cu–O bonding [5].

The curve fitting results are given in table 1.

There are three possibilities for Cu location on ideal α-quartz(0001) surface: atop site above the oxygen, bridge site between two oxygens and three-fold hollow site. The effective coordination numbers in the two directions were calculated

Table 1
Curve fitting results of Cu oxide on α-quartz(0001) [a]

Polarization	Distance (r) (Å)	Effective coordination number (N^*)			
		obs.	calc.		
			atop	bridge	three-fold
CuO	1.96	4			
$E \parallel S$	2.00	3.2	0	1.3	2.5
$E \perp S$	2.02	3.7	3	3.5	3.9
ratio (p/s)		1.2	∞	2.7	1.6

[a] r: ±0.02 Å, N^*: ±0.7.

based on the three models. The experimentally obtained values were compared with the calculated ones. The ratio and absolute values of the observed effective coordination numbers (N^*) for $E \parallel S$ and $E \perp S$ are only explained by the three-fold hollow site model [5].

3.2. Co OXIDE ON α-ALUMINA(0001)

Co oxide on α-alumina prepared from the interaction of $Co_2(CO)_8$ with α-alumina at 313 K, followed by exposure to O_2 showed high activity for CO oxidation as shown in fig. 4 [7]. The catalytic CO oxidation reaction was conducted in a closed circulating system, but the activity was so high that the reaction rate could not be followed. In order to reveal the origin of the high activity of the catalyst, we carried out an asymmetric structure analysis of the active Co oxide on α-alumina(0001) single crystal prepared in the same way. Fig. 5 shows the EXAFS Four-

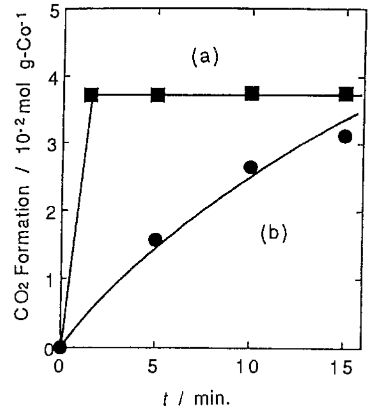

Fig. 4. CO oxidation reaction rates of Co oxide prepared from $Co_2(CO)_8$ (a) and by the impregnation method (b).

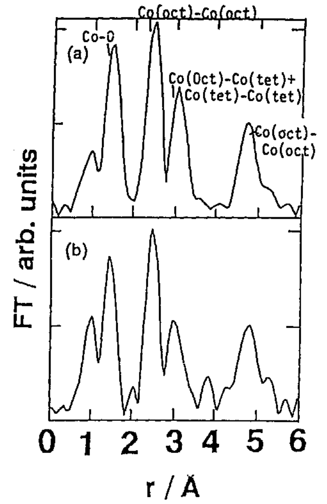

Fig. 5. Fourier transforms for Co oxide for the sample $E \parallel S$ (a) and $E \perp S$ (b).

ier transforms for the Co oxide on α-alumina(0001) in both $E \parallel S$ and $E \perp S$. The peak positions are the same as those for Co_3O_4 [7], indicating the presence of Co_3O_4 spinel particles. However, the peak intensities were different between both directions and also from those of Co_3O_4 powder. Table 2 shows the curve fitting results for the Co oxide on α-alumina(0001). The size of Co_3O_4 spinel particle was estimated to be 9 Å from the coordination numbers of the fourth shell [7]. We have calculated the effective coordination numbers (N^*) based on the several models by changing the exposed planes and the number of the packed layer of the spinel arrangement. The experimental results are explained well and only by the following model as shown in fig. 6 where the $Co_3O_4(001)$ plane with seven layers grew parallel to the α-alumina(0001) plane.

3.3. Pt_4 ON α-ALUMINA(0001)

Catalytic properties of supported metal particles are often affected by morphology as well as metal–support interaction. In the case of EXAFS averaged in every direction, strong metal–metal interaction in metal particles hinders weaker metal–

Table 2
Curve fitting results for Co oxide on α-alumina(0001) [a]

Polarization	Co–O		Co–Co		Co–Co		Co–Co	
	N^*	r	N^*	r	N^*	r	N^*	r
$E \parallel S$	4.2	1.94	6.9	2.86	9.3	3.42	3.1	4.96
$E \perp S$	5.2	1.92	6.0	2.85	7.1	3.42	2.7	4.97

[a] For Co–O; r: ±0.02 Å, N^*: ±0.5; for Co–Co; r: ±0.02 Å, N^*: ±0.3.

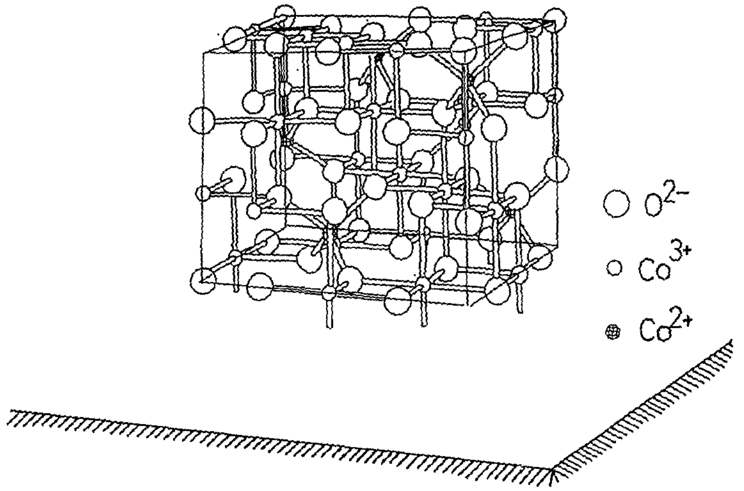

Fig. 6. Co_3O_4 spinel structures in 9 Å-dimension with the (100) plane parallel to α-alumina(0001) surface.

support interaction and it is also difficult to get information on morphological change by means of EXAFS. On the other hand the EXAFS data with $E \parallel S$ and $E \perp S$ for the particle on the single crystal surface studied by means of polarization-dependent total-reflection fluorescence-yield EXAFS method can detect the morphology of particles and its change as well as the metal–support interaction.

For this purpose we prepared Pt_4/α-alumina(0001) by the deposition of $Pt_4(CH_3COO)_8$ on α-alumina at room temperature. Upon supporting, Pt–Pt bonding was cleaved as proved by the disappearance of the Pt–Pt peak. The sample was reduced with H_2 at 393 K in the in situ EXAFS chamber. The EXAFS spectra were measured at room temperature in the presence of H_2. The EXAFS data with $E \parallel S$ revealed that Pt clusters with Pt–Pt bonds were regenerated by H_2 reduction at 393 K [8]. On the other hand, a large peak appeared at 1–2 Å due to the Pt–O bonding in the Fourier transform with $E \perp S$ orientation [8].

This work demonstrates that the possibility of the direct observation of asymmetric structure and its change involving metal–support interaction by the in situ polarization-dependent total-reflection fluorescence yield EXAFS technique. The precise analysis of the EXAFS data will be reported in a following paper [8].

4. Summary

From the above three examples the polarized total-reflection fluorescence EXAFS has the following features.

(1) Structures of metal-sites in two directions parallel and perpendicular to

the support surface are separately measurable and asymmetric structures can be determined.

(2) Structural information about morphology and metal–support interaction can be directly observed.

(3) The detection limit of total-reflection fluorescence yield EXAFS technique is submonolayer (~ 0.3 monolayer).

(4) In situ experiments are possible using the in situ chamber shown in fig. 2.

The fluorescence-yield EXAFS spectra are sometimes interrupted by the diffraction peak form the bulk crystal, but the position of the diffraction peak can be changed outside the EXAFS region by rotating the crystal around the surface normal.

Acknowledgement

The authors express their thanks to Professor M. Nomura in Photon Factory for his helpful advice.

References

[1] Y. Iwasawa, K. Asakura, H. Ishii and H. Kuroda, Z. Phys. Chem. NF. 144 (1985) 105; Y. Iwasawa, Adv. Catal. 35 (1987) 87.
[2] D.C. Koningsberger and R. Prins, eds., *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (Wiley–Interscience, New York, 1988).
[3] S.M. Heald, E. Keller and E.A. Stern, Phys. Lett. A 103 (1984) 155.
[4] M. Shirai, T. Aruga, K. Asakura, M. Nomura and Y. Iwasawa, to be published.
[5] M. Shirai, K. Asakura and Y. Iwasawa, Chem. Lett. (1992) 1037.
[6] R. Sekine and M. Kawai, Appl. Phys. Lett. 56 (1990) 1466.
[7] M. Shirai, K. Asakura and Y. Iwasawa, Catal. Lett. 15 (1992) 247.
[8] M. Shirai, W.-J. Chun, K. Asakura and Y. Iwasawa, to be published.