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In - situ EXAFS Observation of the Molecular Reaction Intermediate for NO - H_2 Reaction on Highly Active Rh - Sn / SiO_2 Catalysts

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In - situ EXAFS technique was successful by applied for the first time to observe the molecular reaction intermediate for NO - H_2 reaction on highly active Rh - Sn / SiO_2 catalysts. The EXAFS data, with the aid of FTIR, revealed the existence the bent - type NO with the bond distance of 0.256 nm with Sn atoms (Rh - NO ••• Sn) on the bimetallic surface in the steady - state reaction conditions. The tilted NO was dissociated to form Sn - O bond at 0.205 nm.

We have found that Rh - Sn / SiO_2 catalysts which were prepared by the selective reaction of $Sn(CH_3)_4$ with Rh metal particles on SiO_2 at 423 K, followed by reduction with H_2 at 573 K, have much higher activities for NO-H_2 reaction and NO dissociation than Rh / SiO_2 and coimpregnation Rh - Sn / SiO_2 catalysts.[1] The catalytic activity of Rh - Sn /SiO_2 for NO - H_2 reaction increased with an increase of Sn content in the range of Sn / Rh ≤ 0.4, showing an S - shape dependency. At Sn / Rh = 0.4, the activity became highest and the turnover frequency (TOF) at 373 K was 75 times as high as that of Rh / SiO_2. The surface structure and composition of Rh - Sn / SiO_2 have been characterized by means of EXAFS, TEM and adsorption measurements.[2] The high catalytic activity of Rh - Sn / SiO_2 was referred to the unique Rh - Sn bimetallic ensemble structure as shown in Fig. 1(a), where a Rh atom is surrounded by six Sn atoms.[2] This geometry provides a preferable arrangement to make Sn ••• O distance (Rh - NO ••• Sn) shorter, because the Sn atoms are protruded from the Rh - atom level at the surface.[3] In this article we report the first EXAFS observation of the molecular reaction intermediate for NO - H2 reaction on Rh - Sn / SiO_2 with the aid of FTIR.

Rh / SiO_2 catalyst was prepared by a conventional impregnation method using a methanol solution of $RhCl_3 \cdot 3H_2O$ followed by reduction with H_2 at 573 K. The sample was interacted with $Sn(CH_3)_4$ to produce the Rh - Sn / SiO_2 catalysts. NO - H_2 reaction was carried out under NO : H_2 = 2.6 kPa : 13.3 kPa at 373 K. *In - situ* EXAFS spectra were measured at BL-6B and 10B stations of the Photon Factory in the National Laboratory for High Energy Physics (Proposal No. 90003 and 92008). The samples were treated *in - situ* in a closed circulating system and transferred to an EXAFS cell without contacting air. EXAFS spectra were measured at room temperature. EXAFS data were collected in a transmission mode using a Si (311) channel - cut crystal monochromator and analyzed by a curve - fitting technique, using the empirical parameters extracted from SnO_2 for Sn - O and the theoretical phase shift[4] and the empirical backscattering amplitude function extracted from Rh metal for Sn - Rh or - Sn (Sn - Rh and Sn - Sn can not be discriminated by present EXAFS analysis because of the similar atomic number of Rh and Sn).

Figure 2 shows the Fourier transforms of Sn K-edge EXAFS spectra for Rh - Sn / SiO_2 (Sn / Rh = 0.45). After H_2 reduction at 573 K a peak assignable to Sn - Rh or -Sn (0.270 nm) was observed. In addition, two peaks at 0.15 nm and 0.20 nm (phase shift uncorrected) were observed during NO - H_2 reaction (Fig. 2(b)). Exposure of Rh - Sn / SiO_2 to O_2 at room temperature showed a similar peak to the first peak in the Fourier transform. The second peak disappeared by evacuation at 573 K after NO - H_2 reaction at 373 K (Fig. 2(c)).

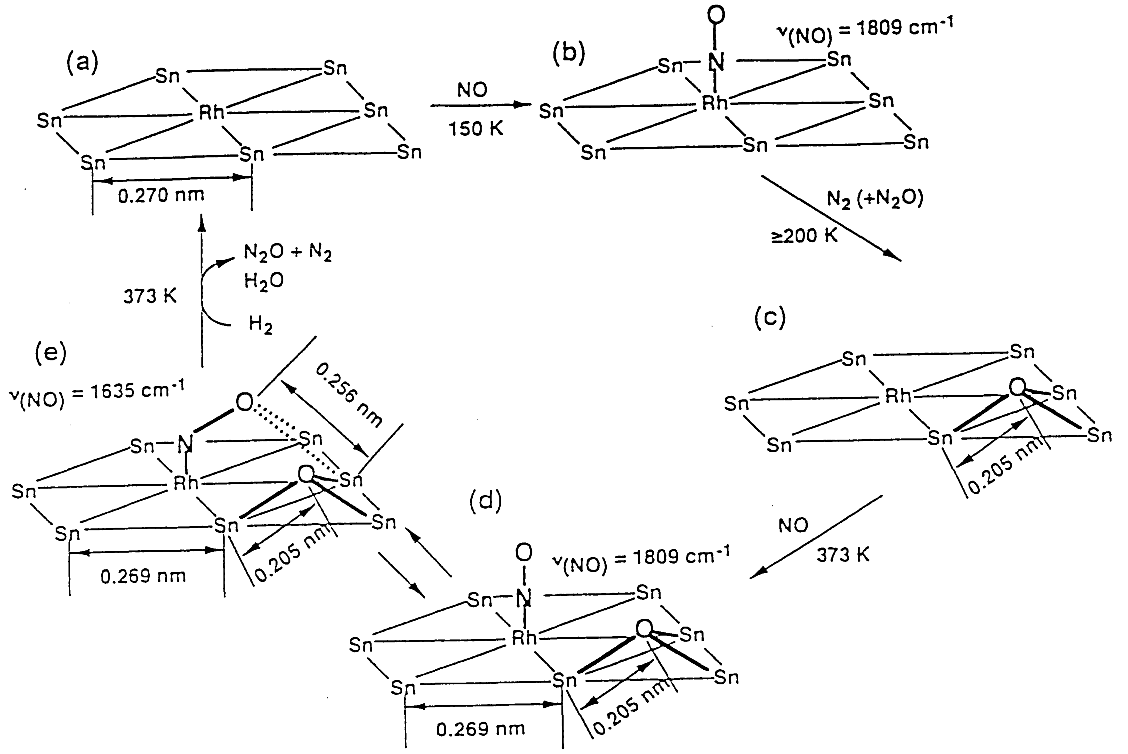

Fig. 1. Reaction steps and intermediates involved in catalytic NO - H_2 reaction, characterized by EXAFS and FTIR.

To examine the origin of the first and second peaks FTIR spectra during NO - H_2 reaction at 373 K and after evacuation at 573 K were measured by JASCO FT - IR 7000 spectrometer.[3] Under the reaction conditions two ν (NO) stretching peaks at 1809 cm^{-1} and 1635 cm^{-1} were observed. The 1805 - cm^{-1} peak is assigned to linear NO species adsorbed on Rh atoms.[5] This is because Sn can not adsorb NO molecules. Both peaks disappeared by heating to 573 K in vacuum (TPD), evolving mainly N_2 with a small amount of N_2O and leaving O atoms at the catalyst surfaces. The behavior of the adsorbed NO species in FTIR and TPD spectra coincides with the increase of the first peak and the disappearance of the second peak in the EXAFS Fourier transform (Fig. 2(c)). When the surface heated to 573 K was exposed to H_2 (13.3 kPa) at 373 K, the Fourier transform (a) of Fig. 2 was reproduced, accompanied with the formation of H_2O. The curve fitting analysis revealed that the first peak is one due to Sn - O bond at 0.205 nm as shown in Table 1. The bond length is similar to 0.206 nm for SnO_2. These results demonstrate that NO instantaneously dissociates on Rh - Sn / SiO_2 at 373 K to form surface O atoms which were characterized by the first Sn - O peak in the Fourier transform (Fig. 2).

On the other hand, the second peak in the Fourier transform corresponds to molecularly adsorbed NO which exhibits the low - frequency ν (NO) peak at 1635 cm^{-1}. Exposure of Rh - Sn / SiO_2 to NO at 150 K showed only a peak at 1809 cm^{-1}, which suggests that the 1635 - cm^{-1} peak is not attributed to two - fold bridge

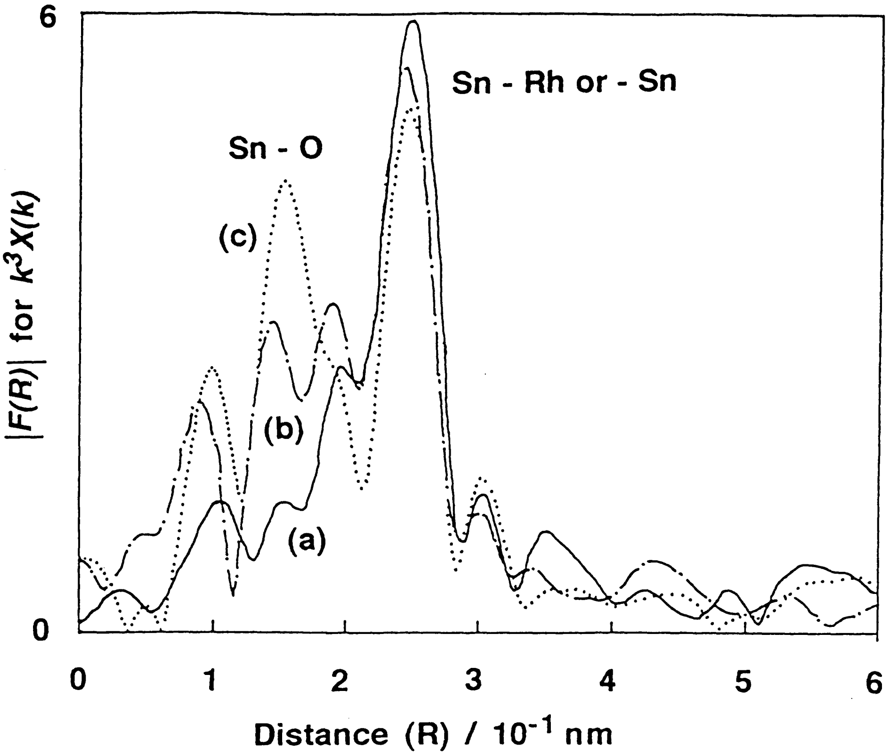

Fig. 2. Fourier transforms of Sn K - edge EXAFS spectra for Rh - Sn / SiO_2 (Sn / Rh = 0.45); (a) reduced sample, (b) in NO - H_2 reaction conditions (P_{NO} = 2.6 kPa, P_{H_2} = 13.3 kPa, 373 K), (c) sample heated to 573 K under vacuum after (b). Fourier transform range: 30 - 120 nm^{-1}.

Table 1. Curve fitting results of Sn K-edge EXAFS on Rh - Sn / SiO_2 (Sn / Rh = 0.45)

	Backscattering atom	N a)	R b) / nm	ΔE_0 c) / eV	D.W.d) / nm	R factore) / %
Vacuum	Rh or Sn	5.9	0.270	4.4	0.0109	
	Rh or Sn	2.6	0.290	6.3	0.0114	4.0
NO - H_2	O	1.0	0.205	-0.6	0.0070	
	O	0.4	0.256	0.0	0.0070	
	Rh or Sn	5.7	0.269	2.9	0.0109	
	Rh or Sn	3.1	0.286	2.1	0.0119	2.0

a) coordination number. b) bond length. c) the difference between origins of the photoelectron wave vector. d) Debye Waller factor. e) residual factor.

Fourier transform range: 30 - 120 nm^{-1}, Fourier filtering range: 0.15 - 0.32 nm (Vacuum) or 0.12 - 0.32 nm (NO - H_2 reaction).

NO on Rh metal surface, because NO molecules on Rh metal adsorb on two - fold bridge sites more favorably than on a - top sites .[6, 7] By heating to 250 K, the low - frequency peak appeared. At this stage the Sn - O bonds (0.205 nm) are formed as proved by N_2 and N_2O desorption. The low - frequency peak was observed on only the surface partially oxidized as a result of NO dissociation as shown in Fig. 1(e). This surface showed the first and second Fourier transform peaks. These results suggest that the 1635 - cm^{-1} peak is assignable to a bent - type adsorbed NO which is characterized by the second peak in the Fourier transform. In fact, the second peak was analyzed to be Sn - O bonds at 0.256 nm by the curve fitting method as shown in Table 1. It has been demonstrated that the oxygen atom of CO adsorbed on bimetallic catalysts interacts with neighboring transition metal cations by FTIR.[8, 9] From these results, we propose the structure of the reaction intermediate for NO - H_2 reaction on Rh - Sn / SiO_2 catalysts in Fig. 1(e). The role of Sn atoms in the catalysis of Rh - Sn / SiO_2 is to remarkably promote NO dissociation through the Sn - O bonding at 0.256 nm. The resultant adsorbed oxygen atoms on Sn atoms were easily removed by H_2 reduction at 373 K.[3]

Another interesting feature of the Rh - Sn bimetallic surface is the observation of the second - nearest Sn - Rh bonds (0.286 nm) as shown in Table 1. The detailed analysis of the third peak in the Fourier transform will be reported in the following paper,[3] but the observed EXAFS data were well reproduced by the two - wave fitting analysis. These results suggest the relaxed surface structure in which the distance between the top layer and the second layer (0.243 nm) is longer than the layer separation in the Rh fcc bulk (0.219 nm). The structural relaxation of the bimetallic top - layer has not been reported with monometallic Rh surface.[10] The surface relaxation has also been demonstrated with Sn/Ni, Cu, Pt alloy single crystals by ion scattering spectroscopy.[10] The present study may reenforce the EXAFS technique as a powerful one for *in - situ* characterization of atomic / molecular - level catalytic mechanism.

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