

Characterization of Active Site on Cobalt-Magnesium Oxide by X-Ray Absorption Fine Structure Spectroscopy

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The geometrical order around divalent Co ion of Co-MgO solid solution was found to control the catalytic reactivity of simple decomposition of nitrous oxide as demonstrated by extended X-ray absorption fine structure spectroscopy (EXAFS).

The emission of NO_x is one of the major, worldwide, urgent environmental problems. Nitrous oxide is emitted in nylon production processes and low-temperature-boilers used in power plants, etc. It causes the green house effect and the ozone layer destruction. Due to less public awareness, the catalyst system of nitrous oxide decomposition has not been well developed compared with those developed for nitric oxide reduction, such as V₂O₅/TiO₂ and three way (Pt-Rh-Pd) catalysts. The cobalt-magnesium oxide is known to be effective for simple decomposition of nitrous oxide (which proceeds in the absence of reductant, such as hydrocarbon or ammonia).¹ In terms of thermal stability, the Co-MgO is superior to metal ion in zeolite, such as Cu-ZSM-5 and Fe-NaY (bulk crystalline of Co-MgO *v.s.* zeolite framework). In this paper, the active site structure of Co-MgO catalysts is investigated by extended X-ray absorption fine structure spectroscopy (EXAFS) to elucidate the catalysis of the Co site in gaseous nitrous oxide. By heating to 1173 K, the formation of complete solid solution of Co-MgO was found by EXAFS. EXAFS data including the metrical deviation from complete solid solution when Co content was increased were supported by the other X-ray techniques, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Dioxygen adsorption² and propene oxidation³ on Co-MgO solid solution have been reported. Decomposition of nitrous oxide (6.7 kPa) at lower temperature (473 K) was studied kinetically in the absence/presence of reductant (alkane⁴ or ammonia⁵). Under these conditions, the simple decomposition rate was proportional to the number of surface Co²⁺ ion.⁴ However, it was not the case under lower pressure (0.1 kPa) and higher temperature (873 - 973 K).⁵ The simple decomposition rate of nitrous oxide per Co atom (turnover frequency, TOF) dramatically increases as the decrease of Co content in catalyst. The TOF's at 873 - 973 K at Co content (defined as atomic ratio Co/(Co + Mg)) of 1.9 - 4.4% are several times higher than that at Co content greater than 9.5%.⁶ The sample of smaller Co content (1.9%) gives higher TOF than the sample of Co 4.4%. The simple decomposition of nitrous oxide is believed to proceed through four steps; the adsorption of nitrous oxide on Co cation with oxygen atom of N₂O, the dissociation of N₂O(ads) into N₂ and O(ads), the spillover of O(ads) toward neighboring Mg cation site, and the desorption of dioxygen formed by the coupling of two atomic oxygen.^{1,4,5,6}

The preparation procedure of Co-MgO samples was described in Ref. 5. EXAFS spectra at Co K-edge of Co-MgO were measured at beamline 10B, Photon Factory in KEK. The *k*³-weighted EXAFS oscillation and its associated Fourier

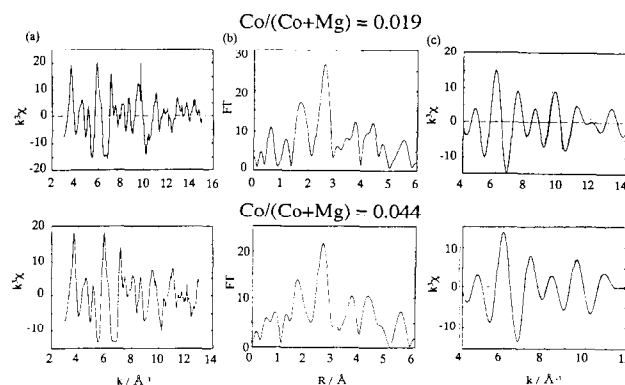


Figure 1. Co K-edge EXAFS for 1.9-Co-MgO and 4.4-Co-MgO. The *k*³-weighted EXAFS oscillation (a), its associated Fourier transform (b), and curve fitting analysis (c).

transform are shown for Co-MgO at Co 1.9 and 4.4% in Figure 1. Samples are denoted, for example, 1.9-Co-MgO and 4.4-Co-MgO. Both the first (at ≈ 1.8 Å) and second (at ≈ 2.6 Å) shell intensities decreased when the Co content increases from 1.9 to 4.4% (Figure 1b). For these two shells, curve fitting analysis was performed⁷ using the amplitude and phase shift parameters generated by FEFF-6.⁸ Detailed analysis procedure has been described elsewhere.^{9,10} The generated parameters of Co-O and Co...Mg bonds from idealized model (Figure 2a) where single Co²⁺ ion substitutes a surface Mg²⁺ site of MgO(100) crystal ($a = 4.2112$ Å) have a peak at ≈ 1.8 Å and ≈ 2.6 Å, respectively (not shown). Hence, the first and second peaks in Figure 1 can be assumed to be due to Co-O and Co...Mg bonds, respectively, and the EXAFS was fit with these two parameters.

The best fit results for 1.9-Co-MgO are at distance $r_{\text{Co-O}}$ of 2.103 Å with coordination number (*N*) of 4.2 and the $r_{\text{Co...Mg}}$ of 2.968 Å with the *N* of 14 (Figure 1c, upper column). These values demonstrate that the binary system constitutes solid solution¹¹ at this Co content. The $N_{\text{Co-O}}$ and $N_{\text{Co...Mg}}$ values are 5 and 8, respectively, if the Co²⁺ distributes at the MgO(100) surface while they are 6 and 12, respectively, if the Co²⁺ substitutes the Mg²⁺ site inside the MgO lattice. Based on EXAFS analysis, Co²⁺ should distribute as isolated at MgO surface and/or in bulk. Note that the Co K-edge oscillation is similar to Mg K- or Ni K-edge oscillation of MgO or Ni-MgO sample in Ref. 12, strongly suggesting isolated Co²⁺. Observed high BET surface area (19 - 39 m²g⁻¹) for 1.9- and 4.4-Co-MgO is consistent with atomic dispersion of cobalt. The $r_{\text{Co...Mg}}$ value is near the expected value (2.974 Å) estimated from the obtained $r_{\text{Co-O}}$ value and simple cubic lattice. The reason of large $N_{\text{Co...Mg}}$ value is unclear, but the distortion of lattice around Co²⁺ may be related.

The theoretically-generated EXAFS of Co-MgO solid

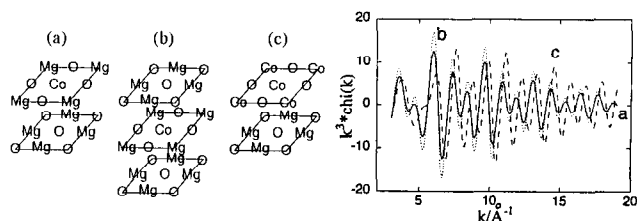


Figure 2. Theoretically-generated Co K-edge EXAFS oscillations for single, isolated Co^{2+} at MgO surface (—, model **a**) or inside MgO (•••, model **b**), and CoO monolayer on MgO (100) surface (- - - -, model **c**).

solution model are illustrated in Figure 2, right. The **a** and **b** are for single, isolated Co^{2+} at surface or inside MgO , respectively, and **c** is for CoO monolayer on MgO (100) surface with the same bond distance. The EXAFS oscillation for **c** is significantly stronger at higher-wavenumber region (11 - 19 \AA^{-1}) compared to **a** or **b**. The EXAFS of 1.9-Co-MgO is similar to **a** or **b** due to the contribution of neighboring O and Mg atoms. The EXAFS of 4.4-Co-MgO is shown in Figure 1, in lower column. The oscillation (a) is also similar to Figure 2a or **b**. As the models **a** and **b** for calculations consists of Co-O and Co...Mg shells, the Fourier-filtered oscillation for the two shells (Figure 1c) resembles more to theoretical ones (Figure 2a and b). The best fit results for 4.4-Co-MgO are at $r_{\text{Co-O}}$ of 2.107 \AA with the N of 4.2 and at $r_{\text{Co...Mg}}$ of 2.975 \AA with the N of 14 (Figure 1c, lower column). Obtained Co-O distances (2.103 - 2.107 \AA) are reasonable compared to those of CoO (2.130 \AA), Co_3O_4 (1.99, 1.89 \AA), and $\text{Co/Al}_2\text{O}_3$ (1.94 - 2.16 \AA).¹³ No peak due to the Co...Co scattering is detected. These EXAFS data suggest that major part of Co^{2+} is again isolated on/in MgO .

The obtained Co-O distance (2.103 \AA) for 1.9-Co-MgO is similar to that of 2.130 \AA for CoO crystal and $d_{\text{Mg-O}}$ of 2.1056 \AA for pure MgO . The $r_{\text{Co-O}}$ increased to 2.107 \AA for 4.4-Co-MgO. The increase of +0.004 \AA suggests that as the doped cobalt ion increases in MgO the solid solution becomes distorted around Co. The lattice interval $d(100)$ values were estimated to be 2.106 and 2.111 \AA for 0.4-Co-MgO and 4.4-Co-MgO, respectively, by our XRD measurements, supporting the formation of solid solution at Co content up to $\approx 5\%$ based on EXAFS. The $d(100)$ values were 2.110 and 2.116 \AA for 9.5- and 33.6-Co-MgO, respectively. The increasing trend of $d(111)$ value according to the Co increase and their EXAFS data (not shown) suggest that Co ion environment becomes not uniform at the Co concentration of 5 - 35%.

The $r_{\text{Co-O}}$ value slightly increased with the greater Co content based on EXAFS. The Co $2p_{3/2}$ XPS binding energy increases from 779.75 (0.4-Co-MgO), to 781.97 (4.4-Co-MgO), then to 782.45 eV (9.5-Co-MgO).⁶ This trend demonstrates that the increased charge on Co from +2 induces the distortion of solid solution. However, the Co $2p_{3/2}$ and $2p_{1/2}$ XPS peaks shift slightly to lower binding energy (BE) on going from CoO (780.5 eV) to Co_2O_3 (≈ 780.0 eV) or Co_3O_4 powders (779.6 eV).^{14,15} One of the reasons should be different covalency of oxygen with Co among these compounds (*i.e.* the oxygen of

Co_2O_3 or Co_3O_4 is more covalent and better donor than that of CoO). The $2p_{3/2}$ BE for 9.5-Co-MgO is similar to those for more ionic Co in solid (≈ 783.0 and ≈ 782.5 eV for CoF_2 and CoF_3 , respectively¹⁴). In solid solution matrix, the environment of Co ion is similar to that of CoO powder at low Co content ($\approx 2\%$), but the Co-O bonds should become more ionic at higher Co content (5 - 10%), reflected by the increased distance (2.107 \AA at Co 4.4%). The nature of Co-O bonding should be closely related to the catalytic reactivity with N_2O .

The superior TOF for nitrous oxide decomposition (Co content $\approx 2\%$) corresponds to +2 valence state of Co at solid solution surface. As the doped amount of Co increases, the effective nuclear charge on Co increases and the $r_{\text{Co-O}}$ also increases. The adsorption of N_2O on catalyst is believed to be non-selective. Hence, the charge on Co primarily controls the ordered structure of solid solution around Co site and therefore the dissociation step of N_2O into N_2 and $\text{O}(\text{ads})$. The stabilization of reduced state of redox-active site ($\text{Co}^{2+/3+}$) enhanced the catalysis in this study. The second shell in Fourier transform of EXAFS is the probe of active site environment (isolated Co, Co layer, or Co bulk). The EXAFS spectra for isolated Co sites were presented.

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