Nitrous oxide decomposition active site on Ni–MgO catalysts characterized by X-ray absorption fine structure spectroscopy

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A contracted Ni\(^{2+}\) coordination site distorted in the direction of Ni–Mg and Ni–Ni was found to be responsible for catalytic \(\text{N}_2\text{O}\) decomposition when Ni\(^{2+}\) is diluted in a MgO matrix (Ni\(^{2+}/\text{Mg}^{2+}\) atomic ratio \(= 1.0\)) based on a local structure study by nickel K-edge X-ray absorption fine structure spectroscopy.

Nitrous oxide is one of the gases which affects the environment. Catalysts for nitrous oxide decomposition have not been well developed compared with various catalysts for nitric oxide decomposition.\(^1\) Nickel–MgO\(^2\) and cobalt–MgO\(^3,4\) are reported to form solid solutions. Metal ion-exchanged zeolites have been reported to be unstable to the effects of formed water during NO or \(\text{N}_2\text{O}\) decomposition reactions. A thermally and water-stable Co–MgO solid solution has been applied to \(\text{N}_2\text{O}\) decomposition.\(^5\) The formation of an fcc structure-based solid solution was demonstrated by EXAFS (extended X-ray absorption fine structure) within the range of Co atom\% \([\text{i.e. Co}/(\text{Co} + \text{Mg}) \times 100]\) of 0–5. However, a severe decrease of catalyst surface area and activity was found when the cobalt content exceeded ca. 10 atom\% owing to the formation of the \(\text{Co}_3\text{O}_4\) spinel phase.\(^6\) Herein, the structure of Ni–MgO catalysts was investigated by EXAFS, XANES (X-ray absorption near-edge structure) and XRD (X-ray diffraction). Solid solution formation and the correlation between the local coordination structure of Ni ions and \(\text{N}_2\text{O}\) decomposition reactivity are discussed.

Powders were prepared by the impregnation of nickel nitrate into MgO and were heated in air at 1173 K for 24 h and in H\(_2\) at 573 K for 1 h. With increase of nickel concentration, the BET surface area monotonously decreased from 50 m\(^2\) g\(^{-1}\) (MgO) to 1 m\(^2\) g\(^{-1}\) (Ni\(_{50.0}\)O\(_{2}\)) per unit BET surface area increased linearly from 2 m\(^2\) g\(^{-1}\) (Ni\(_{1.5}\)O) to 51 m\(^2\) h\(^{-1}\) m\(^{-1}\) (MgO) to 51 m\(^2\) h\(^{-1}\) m\(^{-1}\) (Ni–MgO, Ni 50.0 atom\%) and, then gradually decreased to 22 m\(^2\) h\(^{-1}\) m\(^{-1}\) (Ni\(_{1.5}\)O) at 873 K in a flow system (flow rate 100 ml min\(^{-1}\)).

Normalized Ni K-edge XANES spectra for Ni–MgO catalysts and NiO are shown in Fig. 1A.\(^3\) The rising edge was always within 8339.4–8339.8 eV, demonstrating the valence state of nickel was +2 in the range of Ni 1.5–100 atom\%. As the nickel content increases, the two peaks at 8342 and 8355 eV gradually decreased. The peaks at 8362 and 8389 eV for Ni 1.5 atom\% \([\text{Fig. 1A(a)}]\) gradually shifted, and finally reached 8365 and 8398 eV, respectively, for NiO \([\text{Fig. 1A(f)}]\). The peak intensity at 8389–8398 eV gradually decreased.

These experimental spectra were compared to XANES data generated by \textit{ab initio} calculations. A code FEFF8 was applied to fcc-based model clusters within 6.0 Å from the absorbing Ni atom in self-consistent field (SCF) and multiple scattering calculation modes.\(^7\) The imaginary optical potential used in the calculations of the exchange-correlation potential was fixed to 1.5 eV. The XANES spectrum was generated for an isolated Ni\(^{2+}\) model which contains only one Ni\(^{2+}\) ion at the center of a MgO cluster matrix (Fig. 1B, solid line). The peaks at 8324, 8349 (main peak) and 8389 eV in the XANES of Fig. 1A(a) (Ni 1.5 atom%) were reproduced in the spectra by FEFF8, but the calculated peak at 8359 eV did not correspond to any peaks in Fig. 1A. The gradual decrease in the peaks at 8342 and 8389 eV with increase of Ni\(^{2+}\) content was reproduced by FEFF8 (Fig.

## Scheme 1

Ni–MgO models. Model A: Ni 25 atom\% unit cell model. Model B: Ni 50 atom\% unit cell model. Half of the unit cell is drawn for B. All XANES calculations using FEFF8 were performed for complete (undistorted) fcc coordinates.

## Fig. 1

(A) Ni K-edge XANES for Ni–MgO for Ni atom\% of 1.5(a), 4.4(b), 9.5(c), 33.6(d) and 50.0(e) as well as for NiO(f). (B) Ni K-edge XANES generated by FEFF8 for Ni\(^{2+}\) isolated in MgO (B, —) or at surface of MgO (B, ---), models A and B and for NO (C).

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Table 1 K-edge EXAFS curve fitting results for Ni-MgO catalysts and NiO

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<th>Entry</th>
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<th>N</th>
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<th>Δ(σ²)/10⁻³ Å²</th>
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<th>R(Å)</th>
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* R² = |∫k³|k²|χ(obs.)/dk², |∫k³|k²|χ(phantom)/dk².* According to X-ray crystallography.

1B and C). The peak at 8359 eV in Fig. 1B shifted to 8362 eV for models A and B (Scheme 1) and then to 8365 eV for the NiO model (Fig. 1C). Based on these trends (peak position and intensity), the local structure of Ni²⁺ in Ni-MgO (Ni 1.5 atom% ) corresponds to model A. The experimental spectra for Ni-MgO (Ni 4.4 and 9.5 atom%) were similar to theoretical XANES for model B. The spectra for Ni 33.6 and 50.0 atom% [Fig. 1A(d), (e)] were more similar to theoretical XANES for model B than that for NiO (Fig. 1C). Each peak in the theoretical XANES spectra for the surface isolated Ni²⁺ model was smeared out (Fig. 1B, dotted line), and did not resemble any spectra in Fig. 1A. Hence, impregnated nickel appears to be distributed statistically inside the MgO matrix and less appears at the MgO surface. Although imaginary optical potential values and Debye-Waller factors were varied, the shoulder peak at 8355 eV in Fig. 1A was not reproduced in theoretical XANES spectra.8

Models with locally contracted Ni²⁺ sites (Table 1, entries c-e) shows significantly different Ni-..Mg and Ni-..Ni distances (2.97–2.94 Å in the whole range of Ni (0.02–100 atom%) of ref 12. The lower calculation temperature of Ni-MgO samples (773 K)12 may be the reason for this discrepancy, compared to the temperature of 1173 K used in this work and 1473 K in ref 3. Solid solution formation from supported NiO particles over MgO was suggested to proceed at >1073 K.2

The reason for the dependence of N₂O decomposition rates on Ni²⁺ content in catalysts can be addressed based on the determined Ni²⁺ local structure. Contracted Ni²⁺ sites at the surface are responsible for the dissociation of the NiO–O bond. As the nickel content increases, the number of contracted Ni²⁺ site increases and therefore the Ni₂ formation rate per unit BET surface area increases to Ni 50 atom%. The next elementary step, O(ads) + O → O₂, relates to the activity decrease above Ni 50 atom%. An isotopic study utilizing ¹⁸O labeling of the catalyst surface and ¹⁸O/¹⁰O results in exclusive ¹⁸O/¹⁰O formation, i.e. the step O(ads) + O(surface) → O₂. The Ni²⁺ local coordination for a Ni content of 50.0 atom% (Table 1, entry e) corresponds to model B (Scheme 1). The rate of ¹⁸O/¹⁰O formation was in the order, Ni-MgO (Ni 50.0 atom%) > MgO > NiO, suggesting that surface oxygen bonded to Mg²⁺ is more reactive and diagonal distortion of Ni-..Mg and Ni-..Ni destabilizes lattice oxygen. The nitrous oxide adsorption was weak and not detected by FTIR. Raman and IR spectroscopy may give further insight of distorted lattice vibration around doped Ni²⁺.13

Notes and references

5 Spectra were measured at the KEK-PF, 7C (99G259) using an Si(111) double crystal monochromator in transmission mode at 290 K.
8 Theoretical difficulties in incorporating the experimental effects of beamline energy resolution may be the reason for this result.
9 T. Yokoyama, H. Hamamatsu and T. Ohia, EXAFS 2.1, The University of Tokyo.
11 Based on (111), (200), (220), (311) and (222) reflections.