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Nanophase-separated Ni$_3$Nb as an automobile exhaust catalyst

Genie in the Egg: a nanophase-separated catalyst emerges out of Ni$_3$Nb alloy precursor to exhibit higher performance than the state-of-the-art Pt catalysts toward the remediation of automobile exhaust.

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Nanophase-separated Ni$_3$Nb as an automobile exhaust catalyst†

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Catalytic remediation of automobile exhaust has relied on precious metals (PMs) including platinum (Pt). Herein, we report that an intermetallic phase of Ni and niobium (Nb) (i.e., Ni$_3$Nb) exhibits a significantly higher activity than that of Pt for the remediation of the most toxic gas in exhaust (i.e., nitrogen monoxide (NO)) in the presence of carbon monoxide (CO). When subjected to the exhaust-remediation atmosphere, Ni$_3$Nb spontaneously evolves into a catalytically active nanophase-separated structure consisting of filamentous Ni networks (thickness < 10 nm) that are incorporated in a niobium oxide matrix (i.e., NbO$_x$ (x < 5/2)). The exposure of the filamentous Ni promotes NO dissociation, CO oxidation and N$_2$ generation, and the NbO$_x$ matrix absorbs excessive nitrogen adatoms to retain the active Ni sites at the metal/oxide interface. Furthermore, the NbO$_x$ matrix immobilizes the filamentous Ni at elevated temperatures to produce long-term and stable catalytic performance over hundreds of hours.

Introduction

The environmental impact of automobile exhaust is becoming a challenge not only for rising countries but also for the global community. Remediation of automobile exhaust relies on catalytic converters consisting of precious metals (PMs) including platinum (Pt). The consumption of PMs is increasing to meet the demands of ground transportation in emerging countries and the tighter emissions limits in advanced countries. Moreover, PM catalysts are required by different technologies, such as polymer-electrolyte membrane fuel cells. The development of PM-free catalytic materials is highly desirable to reduce the use of PMs in the automobile industry due to possible depletion of PMs in the near future.

Earth-abundant 3d metals including nickel (Ni) were once considered for use as automobile exhaust catalysts. However, none of these 3d metals were realistic alternatives to PMs primarily due to their inherent susceptibility to dissociative adsorption of nitrogen oxides (NO$_x$) in the exhaust. Indeed, the adsorption energies of oxygen and nitrogen atoms to the Ni surface are, 470 kJ mol$^{-1}$ (O$_{ad}$-Ni(111))$^9$ and 470 kJ mol$^{-1}$ (N$_{ad}$-Ni(111)),$^{10}$ respectively, which is 10–15% larger than the corresponding values for the Pt surface (i.e., 405 kJ mol$^{-1}$ (O$_{ad}$-Pt(111))$^9$ and 430 kJ mol$^{-1}$ (N$_{ad}$-Pt(111))), respectively.$^{10}$ The 3d metals are readily deactivated when subjected to the exhaust atmosphere because the adatoms form stable blocking layers over the surface that inhibit further catalysis (i.e., catalyst poisoning). Another drawback of the 3d metals for exhaust remediation is their low stability to thermal cycles. Automobile exhaust catalysts are assembled into catalytic converters in the form of supported nanoparticles (particle size < 10 nm). The 3d metal nanoparticles are prone to particle agglomeration via the Ostwald ripening process because their melting points are close to the operation temperatures of catalytic converters (<300 °C for four-stroke gasoline engines). Microscopic investigations including in situ transmission electron microscopy have demonstrated that the catalytic performance of nanophase-separated Ni$_3$Nb is ultimately attributed to filamentous Ni and a NbO$_x$ matrix, which spontaneously emerges on the intermetallic surface in the reaction atmosphere due to selective oxidation of Nb. The NbO$_x$ matrix...
absorbs nitrogen adatoms from the Ni surface to retain the active Ni²⁺ sites for improved NO remediation activity. Moreover, the filamentous Ni forms an agglomeration-tolerant network inside and/or over the surface of the NbO₂ matrix, which results in long-term stable NO remediation for more than 500 hours.

Results and discussion

A Ni₃Nb intermetallic precursor (average particle size: 50 µm) was obtained by powdering Ni₃Nb ingots synthesized by arc-melting elemental metals in a pure argon atmosphere (see Fig. S1 and S2† for characterization data of the different intermetallics including Ni₃Nb: powder X-ray diffraction (pXRD) and hard X-ray photoemission spectra (HAXPES)). The powder of the elemental metals, such as Ni, Pt, Nb and Nb₂O₅, was used as purchased as the control catalysts. Nb₂O₅-supported Ni nanoparticles were also synthesized and used as a control (see ESIT for details).

Each of the catalysts was transferred into a gas-circulation reactor (see Experimental section). An aliquot consisting of 10 kPa of the reactant gas (NO : CO = 1 : 1) was circulated through the catalyst powder at 325 °C. Fig. 1a shows the time course of the gas composition over the Ni₃Nb, Pt, Ni and Nb materials. Pt exhibited a finite NO remediation activity, reaching 7.5% NO remediation 35 min after exposure to the reactant gas. Neither Ni nor Nb promoted NO remediation in 60 min. The Ni₃Nb material exhibited a much higher NO remediation activity than that of Ni, Nb or even Pt, and a NO remediation of 96% was achieved in 11 min.

Fig. 1b shows the results of a long-duration catalytic test for the Ni₃Nb material in a steady flow of a He-balanced reactant gas (5 ml min⁻¹; NO : CO : He = 1 : 1 : 98; 400 °C; feeding rate = 5 cm³ min⁻¹; space velocity = 30 000 h⁻¹). Neither NO nor N₂O was detected in the effluent gas 50 h after the exposure to the catalyst. The Ni₃Nb material promoted NO remediation for more than 500 hours, and this catalyst converted 66 mmol of NO to N₂ (inset of Fig. 1b). Fig. 1c shows the result of catalytic tests conducted at different temperatures after the long-duration test. The CO concentration monotonously decreased with increasing temperature and reached zero at 425 °C. The NO concentration decreased more steeply than the CO concentration because a portion of the NO was converted to nitrous oxide (N₂O) in a temperature range from 175 to 375 °C via the following reaction path: NO + 1/2CO = 1/2N₂O + 1/2CO₂. The N₂O fraction in the effluent gas disappeared at 425 °C or higher temperatures, where the reaction proceeded via the major path (i.e., NO + CO = 1/2N₂ + CO₂).

Fig. 1d shows the turnover frequency (TOF) of the Ni₃Nb material for NO remediation as a function of the inverse of the temperature, which was calculated from the data in Fig. 1c. The number of active sites on the sample surface was determined to be 0.47 μmol g⁻¹ by CO chemisorption at 298 K. The TOF of the Ni₃Nb material was calculated to be 0.075 s⁻¹ at 300 °C, which was higher than that for the commercial Pt catalysts (0.025 s⁻¹) and even higher than that reported for the state-of-the-art Pt–Rh catalysts (0.047 s⁻¹). The Ni₃Nb material can be employed as a rational substitute for traditional PM catalysts for NO remediation based on the high TOF and long-term stability.

To elucidate the origin of the catalytic performance of the Ni₃Nb material, we conducted microscopic investigations including in situ transmission electron microscopy. As shown in Fig. 2a, a low-contrast phase propagated from both the top-left and bottom-right corners of the Ni₃Nb material after exposure to the reactant gas (NO : CO : Ar = 1 : 1 : 98) at 400 °C (red arrows show the propagation direction of the low-contrast phase; see ESI† for the in situ TEM observation). This low-contrast phase consisted of Ni metal and low-crystalline, oxygen-deficient NbOₓ (x < 5/2) with a crystal structure that was identical to that of Nb₂O₅ (see Fig. S3 and S4† for HAXPES and Fig. S5† for pXRD). The Ni₃Nb material after the catalysis was further characterized using high-resolution transmission electron microscopes (TEM and STEM). As expected from the HAXPES and pXRD analyses, the surface layer of the material was consisted of Ni metal and low-crystalline NbOₓ after the gas exposure. Importantly, the Ni phase was not dispersed as isolated nanoparticles on the NbO₅ surface (Fig. 2b, see also Fig. S6f). As shown in the elemental-mapping images using electron energy loss spectroscopy (EELS; Fig. 2c), Ni formed a nanometer-thick filamentous network inside the bulk and/or over the surface to result in a nanophase-separated Ni₃Nb, and the distribution of this network was exclusive to the distributions of Nb or O.

Based on the TEM characterizations, a structural model of the catalytic centre of the nanophase-separated Ni₃Nb catalyst has been determined (Fig. 2d). When exposed to the reaction atmosphere, the intermetallic Ni₃Nb evolves into a nanophase-
Fig. 2 Microscopic characterizations. (a) Evolution of nanophase-separated structures on the Ni$_3$Nb surface exposed to the Ar-balanced reactant gas at 400 °C. The scale bars correspond to 200 nm. (b) Scanning transmission microscope (STEM) image of the nanophase-separated Ni$_3$Nb catalyst. (c) Annular-dark field (HAADF) image and elemental-mapping images of the nanophase-separated Ni$_3$Nb catalyst. (d) Structural model of the nanophase-separated Ni$_3$Nb catalyst. (e) Cross-sectional transmission electron microscope (TEM) images of the nanophase-separated Ni$_3$Nb catalyst after 0.5 h (left) and 550 h of exposure to the reactant gas at 400 °C (right).

The separated structure that consists of filamentous Ni and a NbO$_x$ matrix ($x < 5/2$). The filamentous Ni is ingrained in the NbO$_x$ matrix and partially exposed to the atmosphere. Importantly, the filamentous Ni on the catalyst surface retained both the network structure and thickness even after the 550 h of gas exposure (Fig. 2e, see high-quality images in Fig. S7f). The long-term catalytic performance of the Ni$_3$Nb catalyst (see Fig. 1b) is ultimately due to the stability of the nanophase-separated structure on the surface, where filamentous Ni was immobilized in the NbO$_x$ matrix, preventing thermal agglomeration. Indeed, artificially prepared Nb$_2$O$_5$-supported Ni nanoparticles exhibited lower NO remediation activity and shorter lifetime (Fig. S8f) because the Ni nanoparticles are dispersed over the support surface and not embedded by the Nb$_2$O$_5$ matrix.

In addition, we performed in situ Fourier transform infrared spectroscopy (FTIR) and in situ XPS to elucidate the reaction kinetics behind the activity of the nanophase-separated Ni$_3$Nb catalyst. As shown in Fig. 3a, when subjected to the reaction atmosphere (NO : CO : He = 1 : 1 : 98, 400 °C), the Ni catalyst accepted oxygen adatoms to form Ni$_2$O$^-$ and Ni$_3$O species on the surface. The FTIR peak at 2044 cm$^{-1}$, which was assigned to the CO admolecules on the metallic Ni$^0$ sites, was much less intense than the peaks at 2091 or 2183 cm$^{-1}$ that corresponded to the CO admolecules on the Ni$^+$- or Ni$^{2+}$ sites, respectively. In contrast, CO molecules were adsorbed on the nanophase-separated Ni$_3$Nb at metallic Ni$^0$ sites, resulting in an intense IR absorption at 2071 cm$^{-1}$. No peaks corresponding to either Ni$^+$-CO or Ni$^{2+}$-CO were observed, instead, a single peak corresponding to Nb$^{5+}$-CO was recognized at 2183 cm$^{-1}$. It is important to note that the Ni$^0$–CO band for the nanophase-separated Ni$_3$Nb catalyst had a higher wavenumber (2071 cm$^{-1}$) than the reported Ni$^0$–CO band for the pure Ni surface (2044 cm$^{-1}$). The CO admolecules are more weakly adsorbed on the filamentous Ni than those on the pure Ni surface. These weakly adsorbed CO molecules can migrate over the surface of the filamentous Ni to efficiently scavenge oxygen adatoms.

Fig. 3b shows the results of in situ XPS analysis for a single-crystalline Ni(111) surface (purchased from Surface Preparation Laboratory Co.) subjected to a monolayer of NO adsorption in an ultra-high vacuum (UHV). Intense N 1s- and O 1s photoemission peaks, which correspond to the dissociative adsorption of NO, were observed at 100 °C at binding energies of 397.7 eV and 529.6 eV, respectively. Both the N 1s- and O 1s peaks became weak with increasing temperature and disappeared at around 400 °C due to the desorption of nitrogen and oxygen adatoms, respectively. The Ni 2p emission retained the peak position at 852.8 eV and became more intense as the adatoms desorbed from the surface.

The trend in the NO ad/desorption on the Ni$_3$Nb surface was the NO-adsorbed Ni$_3$Nb surface was located at a binding energy of 396.9 eV at 100 °C, indicating that the NO admolecules dissociated into nitrogen and oxygen adatoms. This N 1s binding energy (i.e., 396.9 eV) is consistent with that for niobium nitride (NbN), which indicates that the nitrogen adatoms are not bound to Ni atoms but to Nb atoms. The N 1s
emission became weaker as the temperature increased from 100
to 400 °C. However, this emission increased in intensity again at
higher temperatures with a maximum at 600 °C.

This behaviour in the N 1s emission indicates that in contrast
to those on the Ni surface, the nitrogen adatoms on the
Ni₃Nb matrix can migrate more deeply into the bulk at
approximately 400 °C than the probing depth of XPS (i.e., <1
nm). The O 1s and Ni 2p emissions exhibited different behav-
iors than that observed for the N 1s emission. The O 1s and Ni
2p emissions were weakened at 600 °C and became intense
again at higher temperatures. This trend was due to the
nitrogen atoms, which migrate into the NbOₓ matrix at 400 °C,
being donated back to the surface of the filamentous Ni at
higher temperatures, resulting in decreased Ni and O
emissions.

Based on the in situ spectroscopic results, we propose
a possible reaction mechanism for the nanophase-separated
Ni₃Nb catalyst (Fig. 4). First, dissociative adsorption of NO on
the surface of the filamentous Ni generates nitrogen and oxygen
adatoms, which coat the exposed surface of the filamentous Ni
(Fig. 4a). The nitrogen adatoms spill over to the surrounding
NbOₓ matrix at the metal/oxide interface, creating active Ni⁰
sites for adsorption of CO molecules. The oxygen vacancy of the
NbOₓ matrix, the existence of which was demonstrated by
HAXPES (Fig. S3†), accommodates the nitrogen atoms due to
the ability of Nb to form N–Nb bonds that are as strong as O–Nb
bonds, resulting in the formation of stable oxynitrides (NbON)
(Fig. 4b). The nitrogen atoms migrate through the NbOₓ matrix
and are donated back to the perimeter of the filamentous Ni
to promote N₂ formation. This process occurs in an analo-
gous fashion to hydrogen spillover from metal nanoparticles
to migrate through the supporting materials (e.g., hydrogen atoms

In conclusion, we have found that nanophase-separated
Ni₃Nb exhibits superior catalytic performance compared to
that of Pt for NO remediation in the presence of CO. This
nanophase-separated Ni₃Nb efficiently catalyses NO remedia-
tion through the promoted absorption/back-donation of
nitrogen atoms at the metal/oxide interface. It is also worth of
noting that the Ni₃@NbOₓ can promote the desired NO reme-
diation even in the presence of oxygen (Fig. S9†). The
nanophase-separated Ni₃Nb is highly tolerant to thermal
agglomeration even during long-term catalysis at elevated
temperatures because the filamentous Ni phase is stably
incorporated in the NbOₓ matrix. The evolution of the
nanophase-separated structures and catalytic functionalities
may not be limited to Ni₃Nb but could be expanded to a broad
range of alloy systems containing elements with different
affinities to oxidative atmospheres, such as Cu and Ni/Mn
alloy materials, to produce more earth-abundant and high-
performance automobile catalysts to help us meet current
environmental challenges.

Notes

T. Tanabe and T. Fujita conducted TEM/STEM characteriza-
tions. T. Tokunaga and S. Arai and Y. Yamamoto carried out in situ
TEM characterization. S. Ueda conducted HAXPES
measurements. Catalytic performance tests were done by T.
Tanabe, T. Imai and H. Abe. T. Tanabe and G. V. Ramesh
prepared control catalysts. In situ XPS was carried out by S.
Nagao, H. Hirata and S. Matsumoto. T. Fujita and H. Abe
equally contributed to this work through direction of whole of
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Fig. 4 Possible reaction mechanism for the Ni₃Nb catalyst. (a)
Nanophase-separated Ni₃Nb catalyst in the exhaust atmosphere. Both
the Ni surface and metal/oxide interface perimeter are occupied by
dissociative NO admolecules. (b) Oxygen vacancies on the NbOₓ
matrix adopt nitrogen adatoms. The nitrogen atoms are donated back
to the metal/oxide perimeter to generate N₂ molecules. (c) CO
molecules are adsorbed at the free perimeter and (d) oxidized to CO₂
by the neighbouring oxygen adatoms.
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