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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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$^0$ 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.

Earth-abundant 3d metals including nickel (Ni) were once considered for use as automotive 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)) and 470 kJ mol$^{-1}$ (N$_{ad}$-Ni(111)), respectively, which is 10–15% larger than the corresponding values for the Pt surface (i.e., 405 kJ mol$^{-1}$ (O$_{ad}$-Pt(111)) and 430 kJ mol$^{-1}$ (N$_{ad}$-Pt(111))), respectively. 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).

Herein, we report that a nanophase-separated structure emerging from an intermetallic phase of Ni and niobium (Nb) (i.e., nanophase-separated Ni$_3$Nb) exhibits significantly higher catalytic performance than that of Pt catalysts for the remediation of one of the most toxic chemical species in exhaust (i.e., nitrogen monoxide (NO)) in the presence of carbon monoxide (CO). 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 NbOₓ 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 ESI† 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-balanaced 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). These Ni₃Nb materials 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 NbOₓ 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-
Kinetics behind the activity of the nanophase-separated Ni<sub>3</sub>Nb catalyst. As shown in Fig. 2b, the Ni<sub>3</sub>Nb catalyst is comprised of filamentous Ni adatoms, which are not embedded by the NbO<sub>x</sub> 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<sub>3</sub>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<sub>x</sub> matrix, preventing thermal agglomeration.

Additionally, filamentous Ni is adsorbed on the nanophase-separated Ni<sub>3</sub>Nb matrix and partially exposed to the atmosphere. The filamentous Ni is ingrown in the NbO<sub>x</sub> 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<sub>3</sub>Nb catalyst is ultimately due to the stability of the nanophase-separated structure on the surface, where filamentous Ni was immobilized in the NbO<sub>x</sub> matrix, preventing thermal agglomeration. Indeed, artificially prepared NbO<sub>x</sub>-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 NbO<sub>x</sub> 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<sub>3</sub>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<sup>2+</sup>O<sup>-</sup> and Ni<sub>2</sub><sup>+</sup>O species on the surface. The FTIR peak at 2044 cm<sup>-1</sup>, which was assigned to the CO adatoms on the metallic Ni<sup>0</sup> sites, was much less intense than the peaks at 2091 or 2183 cm<sup>-1</sup> that corresponded to the CO adatoms on the Ni<sup>2+</sup> or Ni<sup>4+</sup> sites, respectively.<sup>23,24</sup>

In contrast, CO molecules were adsorbed on the nanophase-separated Ni<sub>3</sub>Nb at metallic Ni<sup>0</sup> sites, resulting in an intense IR adsorption at 2071 cm<sup>-1</sup>. No peaks corresponding to either Ni<sup>0</sup>–CO or Ni<sup>2+</sup>–CO were observed, instead, a single peak corresponding to Nb<sup>5+</sup>–CO was recognized at 2183 cm<sup>-1</sup>.<sup>25</sup> It is important to note that the Ni<sup>0</sup>–CO band for the nanophase-separated Ni<sub>3</sub>Nb catalyst had a higher wavenumber (2071 cm<sup>-1</sup>) than the reported Ni<sup>2+</sup>–CO band for the pure Ni surface (2044 cm<sup>-1</sup>). The CO adatoms 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. 3c 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 in 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<sub>3</sub>Nb surface was the NO-adsorbed Ni<sub>3</sub>Nb surface was located at a binding energy of 396.9 eV at 100 °C, indicating that the NO adatoms 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.<sup>26</sup> 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 surface 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 behaviours 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 analogous fashion to hydrogen spillover from metal nanoparticles to migrate through the supporting materials (e.g., hydrogen atoms on Ru[Ca23Al28O64]4+(e−)4). Then, two CO molecules are adsorbed by the free Ni0 sites created by N2 generation (Fig. 4c) and further oxidized by neighbouring oxygen adatoms to form two CO2 molecules (Fig. 4d). The CO2 formation creates four free Ni0 sites at the perimeter of the Ni/NbOx interface where dissociative adsorption of two NO molecules occurs to complete the catalytic cycle.

Conclusions

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 remediation through the promoted absorption/back-donation of nitrogen atoms at the metal/oxide interface. It is also worth of noting that the Ni@NbOx can promote the desired NO remediation 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 characterizations. 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 the research and edition of the manuscript.

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