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## Supporting Information for

# Ammonia synthesis over Co-Mo alloy nanoparticle catalyst prepared via sodium naphthalenide-driven reduction

Yuki Tsuji,<sup>a</sup> Masaaki Kitano,<sup>\*a</sup> Kazuhisa Kishida,<sup>ab</sup> Masato Sasase,<sup>ab</sup> Toshiharu Yokoyama,<sup>ab</sup> Michikazu Hara,<sup>bc</sup> and Hideo Hosono<sup>\*abc</sup>

a. Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan E-mail: kitano.m.aa@m.titech.ac.jp; hosono@msl.titech.ac.jp.

b. ACCEL, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

c. Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

#### **Experimental Section**

#### 2.1. Synthesis of Co-Mo bimetallic catalyst using sodium naphthalenide.

Co-Mo/CeO<sub>2</sub>(NaNaph) was synthesized using sodium naphthalenide by a similar reduction method to that previously reported.<sup>S1</sup> Prior to deposition of the Co-Mo catalyst on CeO<sub>2</sub>, CeO<sub>2</sub> powder (Aldrich, 99.9%) was heated in a vacuum at 3.3 °C min<sup>-1</sup> from room temperature to 600 °C and held for 6 h, followed by cooling to room temperature. The dehydrated CeO<sub>2</sub> powder (1 g) was immersed in THF solution (50 mL) containing CoCl<sub>2</sub> (0.34 mmol, Wako, 97.0%) and MoCl<sub>5</sub> (0.34 mmol, Wako, 99.5%), and the mixed solution was then stirred for 4 h at room temperature. The sodium naphthalenide (NaNaph) solution was prepared by reaction of sodium metal (2.62 mmol, Aldrich, 99.9%) with naphthalene (2.62 mmol, Wako, 98%) in THF (20 mL, Wako chemical, 99.5%) over 24 h. The NaNaph solution was added slowly to the precursor solution containing CeO<sub>2</sub>, CoCl<sub>2</sub>, and MoCl<sub>5</sub>. The solution was then centrifuged and washed with absolute methanol to remove all impurities (e.g. NaCl, naphthalene, THF). Finally, the powder was dried in a vacuum at room temperature.

#### 2.2. Synthesis of reference catalysts.

Co/CeO<sub>2</sub> and Mo/CeO<sub>2</sub> were synthesized using a chemical vapour deposition (CVD) method similar to that previously reported.<sup>52</sup> Co<sub>2</sub>(CO)<sub>8</sub> (Kanto Chemicals, 98.0%) or Mo(CO)<sub>6</sub> (Kanto Chemicals, 95.0%) were mixed with dehydrated CeO<sub>2</sub> and sealed in an evacuated silica tube. The tube was heated under a temperature programme of 2 °C min<sup>-1</sup> up to 40 °C, hold for 1 h, 0.25 °C min<sup>-1</sup> up to 70 °C, hold for 1 h, 0.4 °C min<sup>-1</sup> up to 120 °C, hold for 1 h, 0.9 °C min<sup>-1</sup> up to 250 °C, hold for 2 h, and then cooled to ambient temperature.

Co-Mo/CeO<sub>2</sub>(imp) was synthesized using a simple impregnation method. Briefly, CoCl<sub>2</sub> (0.34 mmol) and MoCl<sub>5</sub> (0.34 mmol) were employed as precursors for Co-Mo particles and dissolved in THF solution (50 mL). Dehydrated CeO<sub>2</sub> (1 g) was introduced into the solution and stirred for 4 h. Thereafter, the suspension was evaporated under vacuum, and the resultant powder was dried over 12 h.

Co<sub>3</sub>Mo<sub>3</sub>N was prepared by the following procedure. MoO<sub>3</sub> (9.14 mmol, Kanto Chemicals, 99.5%) and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (19.58 mmol, Aldrich,  $\geq$ 95%) were dissolved in distilled water (100 mL). This aqueous solution was mixed with an aqueous solution (100 mL) containing Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (9.14 mmol, Wako,  $\geq$ 98%) and stirred at 90 °C for 12 h. The obtained precipitate was filtered and washed with distilled water and ethanol, and the powder was then dried at 80 °C overnight. Subsequently, the sample was calcined at 550 °C for 5 h in an air atmosphere to obtain CoMoO<sub>4</sub>. Nitridation of the CoMoO<sub>4</sub> by ammonolysis was performed using a method described in the literature.<sup>53</sup> The CoMoO<sub>4</sub> was heated in a quartz reactor under an NH<sub>3</sub> gas flow (300 mL min<sup>-1</sup>) from room temperature to 357 °C (at 5.6 °C min<sup>-1</sup>), then to 447 °C (at 0.5 °C min<sup>-1</sup>) and finally to 785 °C (at 2.1 °C min<sup>-1</sup>), which was held for 5 h. The sample was cooled to ambient temperature under an NH<sub>3</sub> flow, followed by a purge with N<sub>2</sub> (100 mL min<sup>-1</sup>) to remove residual NH<sub>3</sub> in the reactor. Before the sample was removed from the reactor, it was passivated at room temperature in a stream of 1 vol% O<sub>2</sub>/N<sub>2</sub> mixture (100 mL min<sup>-1</sup>) for 6 h. The structure of the resultant sample was confirmed by XRD analysis as Co<sub>3</sub>Mo<sub>3</sub>N, as shown in Fig. S7.

#### 2.3. Characterization.

The morphologies of the catalysts were investigated using transmission electron microscopy (TEM; JEM-2010F, Jeol)

and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM; ARM-200F, Jeol). The compositions of the catalyst, including spectral imaging to produce elemental maps, were investigated using an STEM equipped with an energy-dispersive X-ray spectrometer (EDX). The samples were dispersed in hexane, and the suspension was dropped on a carbon-coated copper TEM grid in an argon-filled glove bag. The average particle size and particle size distribution were determined by measuring the sizes of ca. 100 metal nanoparticles in TEM images.

X-ray powder diffraction (XRD; D8 ADVANCE, Bruker) patterns of the catalysts were obtained using Cu K $\alpha$  radiation with a rotating anode at 45 kV and 360 mA in the 2 $\theta$  range from 10° to 80° in 0.02° steps.

Temperature programmed reduction with  $H_2$  ( $H_2$ -TPR) was conducted using a BELCAT-A instrument (MiccrotracBEL, Japan). Prior to measurements, the samples (ca. 250 mg) were heated in an  $O_2$  stream (50 mL min<sup>-1</sup>) up to 350 °C (at 11.7 °C min<sup>-1</sup>), held at that temperature for 30 min, and then cooled to room temperature. The samples were then heated (10 °C min<sup>-1</sup>) in a stream of 4.8%  $H_2$ /Ar mixture, and the  $H_2$  consumption was monitored with a mass spectrometer (Bell Mass, MiccrotracBEL, Japan).

X-ray photoelectron spectroscopy (XPS; ESCA-3200, Shimadzu) measurements of Co 2p, Mo 3d, N 1s, Ce 3d, O 2p, Na 1s and Cl 2p were performed using Mg K $\alpha$  radiation at <10<sup>-6</sup> Pa (applied bias voltage to X-ray source of 8 kV). Each spectrum was analyzed using Casa XPS software with Shirley background correction. The binding energy of each spectrum was corrected by reference to the Au 4f<sub>7/2</sub> peaks of gold deposited on the sample. Before XPS measurement, the pelletized sample was placed on the sample holder in a glove box filled with Ar gas. Then, the sample holder was transferred to analysis chamber of XPS apparatus using vacuum chamber which directly connects between the glove box and the analysis chamber of XPS apparatus to avoid the oxidation of the catalyst surface.

The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were estimated using an automatic gas adsorption instrument (BELSORP mini II, MiccrotracBEL, Japan) to measure nitrogen adsorption–desorption isotherms at -196 °C.

The Co and Mo content in the catalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; ICPS-8100, Shimadzu).

#### 2.4. Ammonia synthesis reactions.

Ammonia synthesis reactions were conducted in a silica glass or a stainless steel flow reactor. Under typical reaction conditions, the catalyst was heated from ambient temperature to 400 °C (at 3.3 °C min<sup>-1</sup>) under N<sub>2</sub>+H<sub>2</sub> flow (H<sub>2</sub>/N<sub>2</sub> =3), held at that temperature for 2 h, and then the ammonia produced was monitored. In another case, the catalysts were pretreated from ambient temperature to 600 °C (at 3 °C min<sup>-1</sup>) in N<sub>2</sub>+H<sub>2</sub> flow under a pressure of 0.1 MPa, which was maintained for 6 h. After the pretreatment, the catalysts were cooled to 400 °C over 1 h and held at 400 °C for 2 h.

The concentration of ammonia in the stream that left the catalyst bed (0.05 g) was monitored under steady-state conditions of temperature (300-400 °C), gas flow rate (60 mL min<sup>-1</sup>) and pressure (0.1 to 0.9 MPa). The reaction orders with respect to N<sub>2</sub> and H<sub>2</sub> were obtained at a constant flow rate (60 mL min<sup>-1</sup>) using Ar gas as a diluent, and that for NH<sub>3</sub> was determined with  $(3H_2 + N_2)$  by changing the synthesis gas flow rate.<sup>S2</sup> The ammonia produced was trapped in a 5 mM sulfuric acid solution. The amount of NH<sub>4</sub><sup>+</sup> generated in the sulfuric acid solution was determined using ion chromatography (Prominence, Shimadzu) with a conductivity detector.

## **Supplementary Results**

Table S1 Amounts of Co and Mo in Co-Mo/CeO<sub>2</sub>(NaNaph) determined by ICP-AES analysis.

Catalyst	Co (wt%)	Mo (wt%)	Co/Mo atomic
			ratio
Co-Mo/CeO <sub>2</sub> (NaNaph)	1.41	2.80	1.2

**Table S2** Catalytic performance of Co-Mo/CeO<sub>2</sub>(NaNaph) and Co<sub>3</sub>Mo<sub>3</sub>N for ammonia synthesis at 400 °C and 0.1 MPa.

Catalyst	Particle size of Co-Mo (nm)	$^{b}$ NH $_{3}$ synthesis rate ( $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> )	<sup>c</sup> NH <sub>3</sub> synthesis rate (µmol g <sup>-1</sup> h <sup>-1</sup> )	<sup>d</sup> TOF (x10 <sup>3</sup> s <sup>-1</sup> )
Co-Mo/CeO <sub>2</sub> (NaNaph)	4.0	782.9	18640	1.10
Co <sub>3</sub> Mo <sub>3</sub> N <sup>e</sup>	32.3 <sup><i>a</i></sup>	652	672	0.34

<sup>*a*</sup>The particle size was estimated from the surface area of  $Co_3Mo_3N$  (21 m<sup>2</sup> g<sup>-1</sup>). <sup>*b*</sup>Reaction conditions: Catalyst, 0.05 g; synthesis gas,  $H_2/N_2 = 3$  with a flow rate of 60 mL min<sup>-1</sup>; temperature, 400 °C; pressure, 0.1 MPa. <sup>*c*</sup>NH<sub>3</sub> synthesis rate per Co-Mo weight. <sup>*d*</sup>TOF was estimated by average particle size measured using STEM. <sup>*e*</sup>The data for Co<sub>3</sub>Mo<sub>3</sub>N was taken from Ref S4.

Table S3 Apparent activation energy and reaction order for Co-Mo/CeO<sub>2</sub>(NaNaph) and Co<sub>3</sub>Mo<sub>3</sub>N.

Catalyst	<sup>a</sup> Activation energy (kJ mol <sup>-1</sup> )	$N_2$ order	H <sub>2</sub> order	NH₃ order
Co-Mo/CeO <sub>2</sub> (NaNaph)	60.7	0.83	1.01	-0.85
Co <sub>3</sub> Mo <sub>3</sub> N <sup>b</sup>	56.7	0.99	0.80	-1.34

<sup>*a*</sup>The activation energy of Co-Mo/CeO<sub>2</sub>(NaNaph) was measured at 300-400 °C and 0.1 MPa. <sup>*b*</sup>The kinetic data for Co<sub>3</sub>Mo<sub>3</sub>N was taken from Ref. S4.



Figure S1 TEM images of as-prepared Co-Mo/CeO<sub>2</sub>(NaNaph).



**Figure S2** H<sub>2</sub>-TPR profiles for Co/CeO<sub>2</sub>, Mo/CeO<sub>2</sub>, and Co-Mo/CeO<sub>2</sub>(imp) after heat treatment at 600 °C under N<sub>2</sub> and H<sub>2</sub> flow.



**Figure S3** Ammonia synthesis rate (r) over Co-Mo/CeO<sub>2</sub>(NaNaph) as a function of the partial pressure of N<sub>2</sub> and H<sub>2</sub> under atmospheric pressure.  $\alpha$  and  $\beta$  represent the reaction order for N<sub>2</sub> and H<sub>2</sub> in the following equation:  $r = k P_{N_2}^{\alpha} P_{H_2}^{\beta} P_{NH_3}^{\gamma}$ .



**Figure S4** XRD patterns for Co-Mo/CeO<sub>2</sub>(NaNaph) before (a) and after (b) ammonia synthesis reaction. The bottom represents the reference XRD pattern of CeO<sub>2</sub> (JCPDS No.28709).



Figure S5  $H_2$ -TPR profiles for Co/CeO<sub>2</sub>, Mo/CeO<sub>2</sub>, and Co-Mo/CeO<sub>2</sub>(NaNaph) after heat treatment at 600 °C under N<sub>2</sub> and H<sub>2</sub> flow.



Figure S6 XPS Cl 2p spectrum for Co-Mo/CeO<sub>2</sub>(NaNaph) after heat treatment at 600 °C under N<sub>2</sub>+H<sub>2</sub> flow.



**Figure S7** XRD patterns for (a) CoMoO<sub>4</sub> and (b) Co<sub>3</sub>Mo<sub>3</sub>N prepared in this study. The bottom black lines represent the standard diffraction patterns for CoMoO<sub>4</sub> and Co<sub>3</sub>Mo<sub>3</sub>N.

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