Journal of Catalysis 364 (2018) 31–39

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Control of nitrogen activation ability by Co-Mo bimetallic nanoparticle catalysts prepared *via* sodium naphthalenide-reduction

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ARTICLE INFO

Article history:
Received 16 March 2018
Revised 28 April 2018
Accepted 28 April 2018

Keywords:
Co-Mo bimetallic nanoparticle
Ammonia synthesis
Sodium naphthalenide

ABSTRACT

Co-Mo bimetallic nanoparticles (NPs) with various compositions were prepared on a CeO_2 support (Co-Mo/CeO_2) by sodium naphthalenide driven reduction. The Co-Mo/CeO_2 catalyst exhibits much higher activity for ammonia synthesis than monometallic catalysts such as Co/CeO_2 and Mo/CeO_2, and the optimum activity is obtained at Co:Mo = 4:6. X-ray absorption fine structure (XAFS) analyses reveal that Co_3Mo_3N NPs are formed after ammonia synthesis reaction. Nitrogen temperature programmed desorption (N_2-TPD) measurements indicate that the Co-Mo/CeO_2 catalyst possesses a large number of nitrogen adsorption sites with an intermediate nitrogen adsorption energy between that of Co and Mo. Furthermore, nitrogen vacancy sites, which are active sites for N_2 dissociation, are more easily formed on the Co-Mo/CeO_2 catalyst than on bulk-type Co_3Mo_3N. As a consequence, the turnover frequency of the Co-Mo/CeO_2 catalyst is much higher than that of bulk-type Co_3Mo_3N and is comparable to that of the efficient Ru/CeO_2 catalyst.

1. Introduction

The synthesis of ammonia has attracted significant attention because it is an important raw ingredient for the preparation of chemical fertilizers. The Haber-Bosch process is the currently employed industrial method for ammonia synthesis, which uses a promoted iron catalyst and requires high temperatures (400–500 °C) and high pressures (10–30 MPa) [1,2]. Therefore, various alternative catalytic processes have been devised over the past several years [3–6]. For example, ruthenium (Ru)-based catalysts are well known as the most active catalyst for ammonia synthesis [7–10]; however, the high cost associated with this noble metal is a major drawback. Therefore, there is a need for the development of inexpensive non-noble metal catalysts.

Nørskov and co-workers predicted that the Co-Mo catalyst is more active than Fe- and Ru-based catalysts due to its suitable nitrogen binding energy [11,12]. Density functional theory (DFT) calculations suggested that the nitrogen binding energy of pure Co is too weak and that of pure Mo is too strong, which results in low ammonia synthesis activity. However, the nitrogen binding energy of the Co-Mo catalyst is intermediate between Co and Mo, positioned near the most active metal, Ru. It is thus expected that a Co-Mo catalyst would exhibit high ammonia synthesis activity comparable to Ru-based catalyst. According to the phase diagram, Co_3Mo (κ-phase), Co_7Mo_6 (ε-phase), Co_2Mo_3N, Co_3Mo_3N, $CoMoN_2$, and Co_6Mo_6N are possible Co-Mo bimetallic alloys and bimetallic nitrides [13–17].

Cobalt molybdenum nitride (Co_3Mo_3N) was reported to have higher activity than a commercial Fe-based catalyst under specialized conditions [18–20]. The conventional method for the synthesis of the Co_3Mo_3N catalyst is the nitridation of $CoMoO_4$ in ammonia at high temperatures, which leads to the formation of large Co_3Mo_3N particles [21,22]. As a result, the surface area of the Co_3Mo_3N catalyst is relatively low (21 $m^2\,g^{-1}$), which limits the catalytic activity of Co_3Mo_3N. Recent DFT studies demonstrated

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https://doi.org/10.1016/j.jcat.2018.04.029
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that a number of nitrogen vacancies are formed on the surface of Co_3Mo_3N in the temperature range for ammonia synthesis, and these vacancy sites can adsorb and activate N_2 (Mars-van Krevelen type mechanism) [23,24]. Thus, nanosized Co_3Mo_3N catalysts are more suitable for the production of a large amount of surface vacancy sites. Nevertheless, there has been little effort to prepare Co_3Mo_3N nanoparticle (NP) catalysts for ammonia synthesis.

Recently, we have successfully prepared Co-Mo bimetallic NPs on CeO_2 (Co-Mo/CeO_2) by a liquid-phase reduction method using sodium naphthalenide (NaNaph) as a strong reducing agent [25]. Co-Mo/CeO_2 was found to function as an efficient catalyst for ammonia synthesis; however, further effort is required to understand the correlation between the structural and catalytic properties of Co-Mo/CeO_2. It is expected that the N_2 activation ability could be controlled by the composition and size of the Co-Mo metal NPs.

In the present study, Co-Mo/CeO_2 catalysts with various atomic ratios of Co and Mo are prepared via the NaNaph reduction method, which to enable optimization of the nitrogen binding energy. Furthermore, the local structure of the active sites are fully characterized using transmission electron microscopy (TEM), X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS), elemental analysis, H_2 temperature programmed reduction (H_2-TPR), and nitrogen temperature programmed desorption (N_2-TPD) to reveal the relationship between the catalytic activity and structural properties.

2. Experimental section

2.1. Synthesis of the Co-Mo bimetallic catalyst using NaNaph

Co-Mo(X:Y)/CeO_2 was synthesized by a reduction method similar to that previously reported [25]. Before the deposition of Co-Mo catalyst on CeO_2, CeO_2 powder (Aldrich, 99.9%) was heated in a vacuum at 3.3 °C min^{-1} from room temperature to 600 °C and held for 6 h, followed by cooling to room temperature. The dehydrated CeO_2 powder (1 g) was immersed in a solution tetrahydrofuran of (THF; 50 mL) containing $CoCl_2$ (Wako Chemical, 97.0%) and $MoCl_5$ (Wako Chemical, 99.5%) and the mixed solution was then stirred for 4 h at room temperature. The total amount of Co and Mo in Co-Mo(X:Y)/CeO_2 was fixed at 5 wt% and the molar ratio of Co and Mo in Co-Mo(X:Y)/CeO_2 was varied by changing the amount of $CoCl_2$ and $MoCl_5$. The NaNaph solution was prepared by the reaction of sodium metal (Aldrich, 99.9%) with naphthalene (Wako Chemical, 98%) in THF (20 mL, Wako chemical, 99.5%) over 24 h. The molar mass of NaNaph was 1.1 times more than the total molar mass of chlorides. The NaNaph solution was added slowly to the precursor solution containing CeO_2, $CoCl_2$, and $MoCl_5$. The solution was then centrifuged to obtain Co-Mo loaded CeO_2 powder. The Co-Mo/CeO_2 powder was redispersed and stirred in THF solution for 30 min, then the powder was centrifuged. This step was repeated three times. Thereafter, the catalyst powder was three times redispersed/centrifuged in/from absolute methanol to remove all impurities (e.g. NaCl, naphthalene, THF). Finally, the resultant powder was dried in a vacuum at room temperature.

2.2. Synthesis of reference catalysts

Co_3Mo_3N was prepared by the nitridation of $CoMoO_4$ as follows. $CoMoO_4$ was heated in a quartz reactor under NH_3 gas flow (300 mL min^{-1}) from room temperature to 357 °C (at 5.6 °C min^{-1}), then to 447 °C (at 0.5 °C min^{-1}) and finally to 785 °C (at 2.1 °C min^{-1}), which was maintained for 5 h, and the sample was then cooled to room temperature under NH_3 flow, followed by a purge in N_2 (100 mL min^{-1}) to remove residual NH_3 in the reactor. Prior to removal of the sample from the reactor, it was passivated at room temperature in a stream of 1 vol% O_2/N_2 mixture (100 mL min^{-1}) for 6 h.

Ru/CeO_2 was synthesized using the chemical vapor deposition (CVD) method. CeO_2 (Aldrich, 99.9%) and $Ru_3(CO)_{12}$ (Aldrich, 99%) were mixed in an Ar-filled glovebox, and the mixture was then sealed in an evacuated silica glass tube. $Ru_3(CO)_{12}$ was decomposed by heating the silica tube with a following temperature program: 2 °C min^{-1} up to 40 °C, held for 1 h; 0.25 °C min^{-1} up to 70 °C, held for 1 h; 0.4 °C min^{-1} up to 120 °C, held for 1 h; 0.9 °C min^{-1} up to 250 °C, held for 2 h, and cooled to room temperature.

2.3. Ammonia synthesis reactions

Ammonia synthesis reactions were conducted in a silica glass or a stainless steel flow reactor. For Co-Mo(X:Y)/CeO_2 and Co_3Mo_3N, the catalysts were pretreated from room temperature to 600 °C (3.3 °C min^{-1} (RT-400 °C) and 1 °C min^{-1} (400–600 °C)) in $N_2 + H_2$ flow at 0.1 MPa, which was maintained for 6 h. The concentration of ammonia in the stream that left the catalyst bed (0.05 g) was monitored under steady-state conditions of temperature (300–460 °C), gas flow rate (60 mL min^{-1}, WHSV = 72,000 mL g^{-1} h^{-1}), the ratio of N_2 and H_2 (N_2:H_2 = 1:3), and pressure (0.1–0.9 MPa). The ammonia produced was trapped in 5 mM sulfuric acid solution. The amount of NH_4^+ generated in the sulfuric acid solution was determined using ion chromatography (Prominence, Shimadzu) with a conductivity detector. The turnover frequency (TOF) was calculated by following procedure. The metal surface area (SA_{metal}) is calculated based on the assumption that the metal nanoparticles consist of hemispherical clusters. Therefore, SA_{metal} can be calculated as shown in Eq. (1):

$$SA_{metal} = \frac{2\pi r^2}{\frac{2}{3}\pi r^3 \rho} = \frac{3}{r\rho} \tag{1}$$

where r is the average metal radius, and ρ is the density of the metal. This equation can be expressed using the average diameter of metal particle (d) as follows:

$$SA_{metal} = \frac{6}{d\rho} \tag{2}$$

If the metal particles consist of Co and Mo atoms with a ratio of 1:1, SA_{metal} can be calculated as shown in Eq. (3):

$$SA_{metal} = \frac{\left(\frac{1}{2}N_s\sigma_{Co} + \frac{1}{2}N_s\sigma_{Mo}\right)}{m} \tag{3}$$

where N_S is the number of surface metal sites, m is the weight of metal particle, σ_{Co} and σ_{Mo} are the cross-sectional area of Co and Mo atoms, respectively. As a result, N_S can be expressed as Eq. (4):

$$N_s = \frac{12m}{d\rho(\sigma_{Co} + \sigma_{Mo})} \tag{4}$$

TOF can be estimated using Eq. (5):

$$TOF = \frac{number\ of\ ammonia\ formed\ per\ unit\ time}{N_s} \tag{5}$$

2.4. Kinetic analysis

The kinetic analyses of Co-Mo/CeO_2 were performed according to a procedure in the literature [20]. The reaction orders with respect to N_2 and H_2 were obtained at a constant flow rate (60 mL min^{-1}), using Ar gas as a diluent and that for NH_3 was determined with ($3H_2 + N_2$) by changing the synthesis gas flow rate. 0.1 g of catalyst was heated at 400 °C and 0.9 MPa. The constituent gases of the reactant (N_2, H_2, Ar) were as follows in mL min^{-1}: (5, 15, 0), (10, 30, 0), (15, 45, 0), and (20, 60, 0) for NH_3 order;