Cobalt Molybdenum Bimetallic Nitride Catalysts for Ammonia Synthesis

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Cs promoted cobalt molybdenum bimetallic nitride (Co_3Mo_3N) synthesized by nitridation of cobalt molybdate hydrate with ammonia at 973K was stable and more active for ammonia synthesis (15 mmol $h^{-1}g^{-1}$) at 673 K under 3.1 MPa (N_2 + $3H_2$) than a doubly promoted iron catalyst.

Molybdenum catalyst used for ammonia synthesis has not been studied extensively comparing with iron or ruthenium catalyst which has been well developed and used commercially. Because of the high affinity with nitrogen, molybdenum metal is stable as the nitride during the ammonia synthesis reaction.[1] Recently, a new synthesis method of high surface area molybdenum nitride has been reported.[2] The application as the catalysts for ammonia synthesis, Fischer-Tropsch synthesis, hydrodenitrogenation (HDN), and hydrodesulfurization (HDS) has been reported. To improve the catalysis feature, several bimetallic molybdenum nitrides have been studied.[3] Mittasch has already reported that molybdenum becomes more active for ammonia synthesis when alloyed with iron, cobalt or nickel.[4] Electronic and structural state of molybdenum surface must be changed by alloying. Activation of N_2 on molybdenum surface is well known as the structure sensitive reaction.[5] In this study, we tried to establish a new preparation method of monometallic and bimetallic molybdenum nitride for highly active ammonia synthesis catalysts. We also tried to add alkaline compounds, because electron donation to the active sites by alkaline have been known to promote the dissociation of N_2, especially in the case of ruthenium.[6]

Five kinds of high surface area molybdenum nitride catalysts were synthesized by a temperature programmed reaction of molybdenum precursors with flowing ammonia in a quartz reactor following the procedure of Thompson et al.[7] and Loye et al.[8] For γ-Mo_2N, the precursor was heated under flowing ammonia gas (60mL min^{-1}) at 10 K min^{-1} to 623 K, 0.6 K min^{-1} to 723 K, and 3.0 K min^{-1} to 973 K. For Co_3Mo_3N, the sample was heated under flowing ammonia gas (160 ml min^{-1}) at 5 K min^{-1} to 973 K. The nitrides were held at 973 K for 1 h (for γ-Mo_2N) or 6 h (for Co_3Mo_3N) and then quenched to room temperature.

Molybdenum trioxide (MoO_3) was used for the precursor of molybdenum nitride (γ-Mo_2N, **1**). Cobalt-molybdenum oxide mixture was prepared by impregnation of cobalt nitrate (Co : Mo = 0.05 : 1 / mol : mol) in water or by mixing with cobalt oxide (Co_3O_4) (Co : Mo = 1 : 1 / mol : mol). Those two were nitrided and are expressed as γ-Mo_2N-Co (Co : Mo = 0.05 : 1) (**2**) and CoMo mixed nitride (Co : Mo = 1 : 1) (**3**), respectively. Cobalt molybdate ($CoMoO_4$, identified with XRD, 2θ = 25.3, 28.4, 32.4, and 39.6°) and cobalt molybdate hydrate ($CoMoO_4 \cdot nH_2O$, identified with XRD, 2θ = 26.7 and 29.3°) were used for the precursor of cobalt molybdenum bimetallic nitride (Co_3Mo_3N, identified with XRD, 2θ = 35.3, 40.0, 42.5, and 46.5°). Those two were also nitrides. Since the two products had different activity and surface area, those are expressed as **4** and **5**, respectively. Cobalt molybdate was prepared by mixing cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) with ammonium molybdate ($NH_4Mo_7O_{24} \cdot 4H_2O$) and by calcining the mixed powder at 1073 K. Cobalt molybdate hydrate was prepared by addition of cobalt nitrate solution to ammonium molybdate solution and by heating the mixed solution. A blue-purple solid product was isolated by vacuum filtration, rinsed twice with water and once with ethanol, and dried overnight at 423 K.

Alkaline promoted cobalt molybdate hydrates were prepared by impregnating precursor oxides with caesium nitrate (Cs : Mo = 0.02 : 1 or 0.1 : 1 / mol : mol). The nitrided samples are expressed as **5**-CsOH (2%) or **5**-CsOH (10%).[9]

After nitridation, ammonia synthesis was performed in the same apparatus at 673 K under 0.1 MPa with a flow rate of 60 ml min^{-1} of (N_2+$3H_2$).[6] The reaction apparatus and the detection method of ammonia has been reported elesewhere.[10] Since high pressure ammonia synthesis was done in the other apparatus (with a flow rate of 60 mL min^{-1} of N_2+$3H_2$), the catalysts must be moved in the air. Thus, the catalysts were once treated with diluted oxygen (O_2 : He = 1 : 100) (passivation), then, reactivated with the reaction gas at 873 K for 6h. The catalyst weight was 0.4 g. BET surface areas were measured at 77 K using N_2 before and after ammonia synthesis runs.

Figure 1 shows time courses of ammonia synthesis rate at 673 K under 0.1 MPa over 5 kinds of molybdenum nitride catalysts. First, we compare the nitride **1** (γ-Mo_2N), **2** (5% Co added), and **3** (100% Co added). The surface areas of **1**, **2**, and **3**

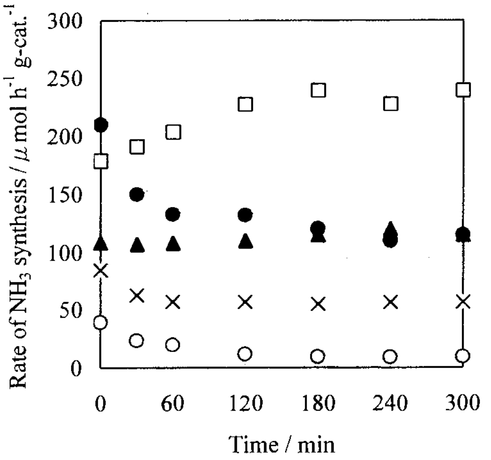

Figure 1. Time course of ammonia synthesis rates at 673 K under 0.1 MPa over 5 kinds of molybdenum nitride catalysts.
○ γ-Mo_2N (**1**), ● γ-Mo_2N-Co (**2**),
× CoMo mixed nitride (**3**), ▲ Co_3Mo_3N from $CoMoO_4$ (**4**),
☐ Co_3Mo_3N from $CoMoO_4$-nH_2O (**5**).

were 186, 194, and 17 m^2g^{-1}, respectively, and little change was observed for each during the reaction. The initial activity of **1**, **2**, and **3** were 35, 210, and 85 μmol $h^{-1}g^{-1}$, respectively. The activity of Co metal powder was very low (6.0 μmol $h^{-1}g^{-1}$). Thus, the addition of cobalt to molybdenum nitride was indeed effective, however, too much addition of cobalt (**3**) was not proper. Another feature of these nitrides is their deactivation, which was not caused by sintering (constant surface area). Surface structural change is suggested during the reaction. Surface and bulk nitrogen atom has been known to be movable during ammonia synthesis on Mo_2N.[1]

The other two Co_3Mo_3N catalysts (**4** and **5**) prepared from $CoMoO_4$ and $CoMoO_4{\cdot}nH_2O$ were more active and stable. The surface areas were 19 and 52 m^2g^{-1}, respectively. And the activities were 109 and 179 μmol $h^{-1}g^{-1}$, respectively. XRD results show that **4** and **5** are composed by Co_3Mo_3N as a main phase. The activity of **5** and **4** were even increased during the reaction, 179 to 239 μmol $h^{-1}g^{-1}$ and 109 to 120 μmol $h^{-1}g^{-1}$ for 5 h, respectively. Contrary to the nitrides **1** to **3**, the surface areas of **5** and **4** were decreased form 52 to 33 m^2g^{-1} and 19 to 14 m^2g^{-1}, respectively. Judging from such low surface areas of Co_3Mo_3N catalysts (**5** and **4**) comparing with γ-Mo_2N catalysts (**2**), specific activity of **5** and **4** must be much higher than that of **2**. Stable Co_3Mo_3N phase is suggested to be responsible to the active surface structure of ammonia synthesis.

Table 1. Ammonia synthesis rates (μ mol h^{-1} g-cat.$^{-1}$) at 673 K under 0.1 MPa of alkaline promoted Co_3Mo_3N (**5**) catalysts

Alkaline	Fresh	Reactivated
none	179.2	652.0
Cs 2 %	404.7	985.6
Cs 10 %	663.5	586.5

To improve the catalytic activity, catalyst **5** (Co_3Mo_3N prepared from $CoMoO_4{\cdot}nH_2O$) was added with alkaline. Table 1 shows ammonia synthesis rate of alkaline added Co_3Mo_3N (**5**) at 673 K under 0.1 MPa. Caesium was found to promote Co_3Mo_3N catalysts. Alkaline compounds were proposed to exist as hydroxides.[5, 6] For the initial activity, the best promotion is observed when alkaline is added to 10 mol% Cs. However, 10 mol% addition of caesium was not proper after the reactivation (passivation and hydrogenation). Interestingly, after the reactivation, the activity of **5** and **5**-CsOH (2%) were increased (from 179 to 652 μmol $h^{-1}g^{-1}$ or from 405 to 986 μmol $h^{-1}g^{-1}$). However, the activity of **5**-CsOH (10%) was almost the same (587 μmol $h^{-1}g^{-1}$). Similar results have been reported for iron catalysts.[11] BET surface area of **5**-CsOH (2%) and (10%) promoted Co_3Mo_3N (fresh catalysts) were 47, 14 m^2g^{-1}, respectively, so addition of alkaline decreased the surface area (from 52 m^2g^{-1}). After the reactivation, BET surface areas of those catalysts **5**-CsOH (2%) and **5**-CsOH (10%), were decreased to 21, 16 and 9 m^2g^{-1}, respectively. The excess alkaline addition must cover the active sites.

For industrial use, the activity under high pressure was measured. Figure 2 shows the synthesis rate as a function of the total pressure over **5**, **5**-CsOH(2%), **5**-CsOH(10%) and a commercial iron catalyst; $Fe\text{-}K_2O\text{-}Al_2O_3$ (C73-1). $Fe\text{-}K_2O\text{-}Al_2O_3$ was activated under the reaction gas flow at 673K for 10 days, because the activity is known to be increased during the reaction. The activity of both Co_3Mo_3N (**5**) and the iron catalyst were increased with increasing the reaction pressure. Especially, 2% caesium promoted Co_3Mo_3N catalyst (**5**) was much more active than the iron catalyst under reaction pressure 0.1–3.1 MPa. (0.6, 3.0, 6.0, and 9.3% NH_3 in exit gas under 0.1, 1.1, 2.1 and 3.1 MPa, respectively) Co_3Mo_3N with and without alkaline was proved to be a stable and more active ammonia catalyst.

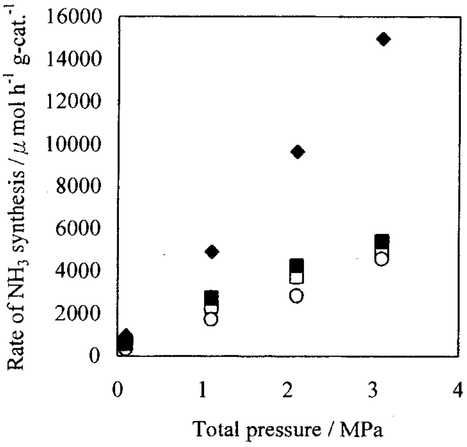

Figure 2. Ammonia synthesis rates at 673 K as a function of the total pressure over Co_3Mo_3N (**5**) catalysts and $Fe\text{-}K_2O\text{-}Al_2O_3$.
□ Co_3Mo_3N, ◆ 2% Cs promoted Co_3Mo_3N,
■ 10% Cs promoted Co_3Mo_3N, ○ $Fe\text{-}K_2O\text{-}Al_2O_3$.

The deep reasoning of the effectiveness of Co_3Mo_3N can not be given here. If the elements are compared, molybdenum is more active than cobalt.[5] Two reasons can be proposed. One is that Mo atom is the active center for N_2 activation, and that the nitride formation and Co incorporation (Co_3Mo_3N) may change electronic and structural state around the Mo atom. The second is that Co-Mo binary sites may be more active than Mo-Mo sites for ammonia synthesis. Alkaline addition can further change the electronic circumstance of those active sites (Mo atoms or Co-Mo binary active sites). These assumption must be clarified by the characterizations such as XAFS, XPS, et. al. in the future. Here, we report that new catalysts containing Co_3Mo_3N is most effective among molybdenum catalysts so far reported, and may be used industrially.

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