

Cobalt Rhenium Binary Catalyst for Ammonia Synthesis

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Co–Re catalyst (Co : Re = 1 : 4) prepared by reduction of cobalt nitrate hydrate and ammonium perrhenate mixture with ammonia at 973 K was very active for ammonia synthesis ($2.4 \text{ mmol h}^{-1} \text{ g}^{-1}$) at 623 K under 3.1 MPa ($\text{N}_2 + 3\text{H}_2$, 60 mL min^{-1}) in spite of extremely low surface area ($< 0.5 \text{ m}^2 \text{ g}^{-1}$).

Rhenium based catalysts have not been studied extensively, since this element was not discovered until 1925 and was not readily available until many years later, or crustal abundance of this element was very low. However, rhenium sometimes attracts researchers because of its special properties (high melting point, hardness, catalytic ability of hydrogenation, and so on). Re metal itself has been paid attention for its intrinsic activity of ammonia synthesis. Somorjai et al. and Asscher et al. have once showed that the single crystal and polycrystalline surface are quite active for ammonia synthesis.^{1–4} Polycrystalline rhenium is more active than the most active crystal plane of iron (Fe(111)), and the reaction rate is remarkably sensitive to the catalyst surface structure ($\text{Re}(0001) < \text{Re}(1010) < \text{Re}(1120) < \text{Re}(1121)$). Thus, the development of high active catalyst based on rhenium can be expected by the similar methods with molybdenum which has structure sensitivity for ammonia synthesis. For the case of molybdenum, alloying with the other transition metal (Fe, Co, and Ni) in the form of nitride was found to be active for ammonia synthesis. $\text{Co}_3\text{Mo}_3\text{N}$ was prepared with sophisticated procedures, but was found to be active and stable.⁵ The purpose of this work is to develop new rhenium catalyst for ammonia synthesis with the other transition metal addition.

Ammonium perrhenate (NH_4ReO_4) was used as the precursors of rhenium metal catalysts. For the mixed metal catalysts, the precursors were prepared by mixing the metal (Fe, Co, and Ni) nitrate and ammonium perrhenate. The samples were heated under flowing ammonia gas (160 mL min^{-1}) at 5 K min^{-1} to 973 K and held at 973 K for 2 h and then quenched to room temperature. The ratios of Co (or Fe, Ni) and Re were 1 : 3, 1 : 4, 1 : 6, and 1 : 9 (mol : mol, Re contents were 75.0, 80.0, 85.7, and 90.0 mol%, respectively), and the samples were expressed as Co–Re3, Co–Re4, Co–Re6, Co–Re9, Fe–Re3, Fe–Re4, Fe–Re6, Fe–Re9, Ni–Re3, Ni–Re4, Ni–Re6, and Ni–Re9, respectively.

After catalysts preparation, ammonia synthesis was performed. The standard reaction condition was at 623 K under 0.1 MPa with a flow rate of 60 mL min^{-1} of ($\text{N}_2 + 3\text{H}_2$). The catalyst weight was 0.4 g. The reaction apparatus and the detection method of ammonia has been reported elsewhere.⁶ Since high pressure ammonia synthesis was done in the other apparatus, the catalyst must be moved in the air. Thus, before the ammonia synthesis, the catalyst must be reactivated with the reactant gas (60 mL min^{-1}) at 623 K for 2 h. High pressure

activity measurement were performed under 1.1, 2.1, and 3.1 MPa at 623K after the reactivation with the reactant gas for Re metal, Co–Re4 catalyst, and Ni–Re4 catalyst. The kinetic analyses on molybdenum nitride catalysts are mainly based on a model described elsewhere.⁷ The constituent gases of the reactant (N_2 , H_2 , He mL min^{-1}) were as follows; (5, 15, 0), (10, 30, 0), (15, 45, 0), and (20, 60, 0) for NH_3 order, (5, 24, 31), (5, 30, 25), (5, 42, 13), and (5, 54, 1) for H_2 order, and (6, 24, 30), (10, 24, 26), (15, 24, 21), and (22, 24, 14) for N_2 order. These analyses were performed for Re metal, Co–Re4 catalyst, and Ni–Re4 catalyst at 623 K under 3.1 MPa.

Figure 1 shows ammonia synthesis rates on the three mixed Re catalysts (Co–Re, Fe–Re, and Ni–Re) as a function of Re content. For Co–Re system, the maximum activity was obtained when Re content was 80.0% (Co–Re4 catalyst). Similar trend was found for Fe–Re system. The rate was increased when Co or Fe was added, although the Re amount was decreased. Contrary to these two systems, the activity of Ni–Re system catalysts did not change between 75.0 and 90.0% Re. Although the activity of cobalt metal was very low ($3 \text{ } \mu\text{mol h}^{-1} \text{ g-cat.}^{-1}$), the addition of cobalt to rhenium was very effective for the activity ($492 \text{ } \mu\text{mol h}^{-1} \text{ g-cat.}^{-1}$ for Co–Re4 catalyst). The addition of iron was also effective, however, the rate over Fe–Re4 catalyst ($275 \text{ } \mu\text{mol h}^{-1} \text{ g-cat.}^{-1}$) was lower than that over Co–Re4 catalyst. Interestingly, the addition of nickel did not improve the activity much ($143 \text{ } \mu\text{mol h}^{-1} \text{ g-cat.}^{-1}$ for Ni–Re4). The surface areas of these five catalysts were too low to be measured by BET method (measurement limit is about 0.5

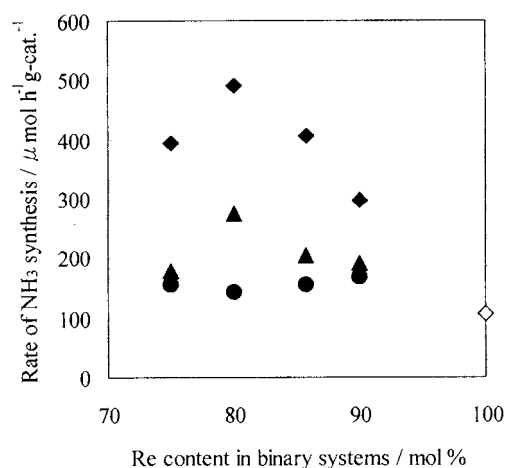


Figure 1. Ammonia synthesis rates at 623 K under 0.1 MPa over Re catalysts as a function of rhenium content in binary systems.

◇ Re, ◆ Co-Re, ▲ Fe-Re, ● Ni-Re.

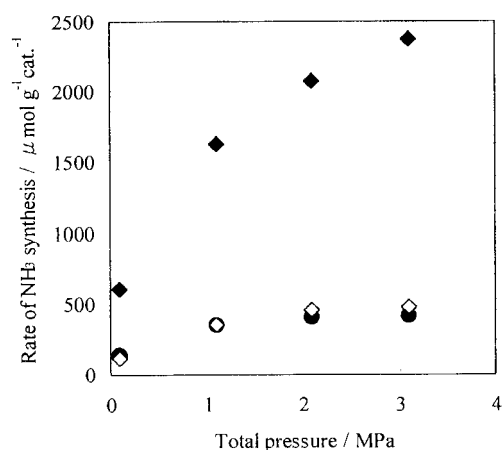


Figure 2. Ammonia synthesis rates at 623 K over Re catalysts as a function of total pressure.
 ◇ Re metal, ◆ Co-Re4 catalyst, ● Ni-Re4 catalyst.

$\text{m}^2 \text{g}^{-1}$ for the used apparatus). H_2 or CO chemisorption measurement was even impossible, thus, TOF can not be calculated. Apparent activation energies over these catalysts were about 14 kcal mol^{-1} , these value were on the same level with $\text{Fe-K}_2\text{O-Al}_2\text{O}_3$ or $\text{Co}_3\text{Mo}_3\text{N}$ catalysts.⁵

Figure 2 shows ammonia synthesis rates at 623 K as a function of the total pressure over 0.4 g of Re metal, Co-Re4 catalyst, and Ni-Re4 catalyst. The catalyst was once moved in air, then, reactivated with the reaction gas at 623 K for 2 h. The rates (120 , 600 , and $143 \mu\text{mol h}^{-1}\text{g}^{-1}$ over Re, Co-Re4, and Ni-Re4, respectively) was not decreased after the reactivation. The rate was increased with increasing the reaction pressure. Especially, the rate over Co-Re4 catalyst at 623 K under 3.1 MPa was $2372 \mu\text{mol h}^{-1}\text{g}^{-1}$, this value was higher than those over $\text{Fe-K}_2\text{O-Al}_2\text{O}_3$ and $\text{Co}_3\text{Mo}_3\text{N}$ (2010 and $2113 \mu\text{mol h}^{-1}\text{g}^{-1}$ at 623 K under 3.1 MPa, respectively).⁵ The activity of Co-Re4 catalyst was surprisingly high considering the low surface area (below $0.5 \text{ m}^2 \text{g}^{-1}$) of this catalyst (BET surface areas of $\text{Fe-K}_2\text{O-Al}_2\text{O}_3$ and $\text{Co}_3\text{Mo}_3\text{N}$ were about $20 \text{ m}^2 \text{g}^{-1}$). On the other hand, the rate over Ni-Re4 at 623 K under 3.1 MPa was $415 \mu\text{mol h}^{-1}\text{g}^{-1}$, and this value was lower than that over Re metal ($480 \mu\text{mol h}^{-1}\text{g}^{-1}$), although Ni-Re4 catalyst was a little more active than Re metal under 0.1 MPa.

Then, the kinetic analysis was performed over these catalyst. Above 1.1 MPa, the increase of the rate was somewhat small. It is guessed that this catalytic behavior is related with the active site retardation. The values of the reaction order for ammonia synthesis on Re, Co-Re4, and Ni-Re4 at 623 K under 3.1 MPa were shown in Table 1. For Re metal, the N_2 order (0.92) was almost 1, thus, the rate determining step on Re catalyst was the activation of dinitrogen, this feature was the same with Fe, Ru, and Mo catalysts. The NH_3 order was negative (-0.82), so it is similar to Fe and Mo catalysts.⁸ The surface of

Table 1. Reaction order for ammonia synthesis on Re catalysts at 623 K under 3.1 MPa

Catalyst	NH_3 order	H_2 order	N_2 order
Re	-0.82	-0.23	0.92
Co-Re4	-0.54	-0.70	0.91
Ni-Re4	-1.23	-0.28	0.91

Re catalyst was retarded by the product ammonia. The H_2 orders of Fe and Mo catalysts were positive, however, the H_2 order was slightly negative (-0.23). It is interesting to find that the surface of Re catalyst was retarded by the reactant hydrogen, but weakly. It is known that the surface of Ru catalysts were retarded by hydrogen strongly.⁸ Thus, the Re catalyst was the intermediate nature between molybdenum and ruthenium catalysts (like the periodicity) as far as hydrogen retardation is concerned. The N_2 order (0.91) on Co-Re4 and Ni-Re4 were almost 1, thus, the rate determining step on these two catalysts was the activation of dinitrogen, too. The NH_3 order (-0.54) on Co-Re4 was less negative and the H_2 order (-0.70) on Co-Re4 was more negative than in the case of Re metal. By the addition of cobalt, the degree of ammonia poisoning was weakened, but at the same time, the degree of hydrogen poisoning was strengthened. However, the NH_3 order (-1.23) on Ni-Re4 was less negative and the H_2 order (-0.28) on Ni-Re4 was more negative than in the case of Re metal. By the addition of nickel, the degree of ammonia poisoning and hydrogen poisoning were strengthened at the same time. Addition of nickel was not effective from the view for kinetics.

The deep reasoning of the effectiveness of Co-Re binary catalyst can not be given here. However, cobalt-rhenium binary catalyst must be studied further, because its activity was found to be quite high, although the surface areas was extremely low. If a high surface area Co-Re binary catalyst can be prepared, the ammonia synthesis under more mild condition can be realized.

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