Novel class of ammonia synthesis catalysts

Claus J. H. Jacobsen

Haldor Topsøe Research Laboratories, Nymøllevej 55, DK-2800 Lyngby, Denmark. E-mail: chj@topsoe.dk

Ternary nitrides Fe₃Mo₃N, Co₃Mo₃N and Ni₂Mo₃N, exhibit high catalytic activities in ammonia synthesis; promotion of Co₃Mo₃N with caesium results in higher activity than that of the commercial multi-promoted iron based catalyst.

During the 20th century the catalytic ammonia synthesis has grown to be among the most important industrial processes. More than 1% of the total global energy consumption is currently used for ammonia production. Therefore, improvements in this process could have a significant impact on the consumption of fossil fuels. Consequently, a continuous effort has been made to improve both the Haber–Bosch process and the promoted iron based catalyst discovered by Mittasch and coworkers. Despite these efforts, the preferred industrial ammonia synthesis catalyst is still a multi-promoted iron catalyst very similar to that developed almost a century ago. It was realized by the group of Haber that both osmium and ruthenium catalysts exhibit high ammonia synthesis activities.[1]

Detailed accounts of the previous work on non-iron catalysts have been published.[2,3] Recently, a promoted ruthenium catalyst supported on a special graphite carrier was introduced in commercial operation.[4,5] However, it is not clear whether the improved activity of such catalysts is justified by the significantly higher cost and shorter life-time relative to the traditional iron catalyst. Clearly, it would be very desirable to develop new, active and stable catalysts that do not contain noble metals. We have found that the ternary nitrides Fe₃Mo₃N, Co₃Mo₃N and Ni₂Mo₃N are active and stable ammonia synthesis catalysts at industrially relevant conditions. Addition of a small amount of Cs to Co₃Mo₃N results in a catalyst with a higher activity than that of the commercial multi-promoted iron catalyst.[6]

Ternary nitrides were obtained by two different routes. The first is based on ammonolysis of solid oxide precursors as reported in the literature.[7] The oxide precursors were obtained by mixing a solution of the desired metal nitrate salt (M = Fe, Co, Ni) with a solution of ammonium heptamolybdate. The mixture was evaporated to dryness and calcined at 400 °C for 2 h. The resulting MMoO₄·xH₂O was heated at 0.1 °C min⁻¹ to 600 °C in a stream of 4.5% NH₃ in 3∶1 H₂–N₂. After cooling to room-temperature it was confirmed by X-ray powder diffraction that pure Fe₃Mo₃N, Co₃Mo₃N and Ni₂Mo₃N were formed when Fe∶Mo = 1, Co∶Mo = 1 and Ni∶Mo = 2/3, respectively. It was also found that if a Ni∶Mo ratio of 1 was used, the X-ray powder patterns could be assigned to a mixture of Ni₂Mo₃N and NiMo alloy and *not* to Ni₃Mo₃N as previously suggested.[8] Alternatively, the ternary nitrides were prepared from high surface area molybdenum nitride obtained by temperature programmed reaction of MoO₃ with NH₃ as described by Volpe and Boudart.[9] The resulting Mo₂N with a surface area of > 200 m² g⁻¹ was successively impregnated with saturated solutions (followed by drying) of the desired metal nitrate solution to obtain the correct stoichiometry. Subsequently, the sample was dried and heated at 0.1 °C min⁻¹ to 600 °C in a stream of 4.5% NH₃ in 3∶1 H₂–N₂. It was confirmed by X-ray powder diffraction that Fe₃Mo₃N, Co₃Mo₃N and Ni₂Mo₃N were also formed by this procedure.

Addition of controlled amounts of caesium nitrate to the catalysts could be achieved either by impregnation of the oxide precursors prior to ammonolysis or directly onto the nitride catalyst before testing.

X-Ray powder patterns were recorded by slow scanning on a Philips vertical goniometer equipped with a θ-compensating divergence slit and a diffracted beam graphite monochromator utilizing Cu-Kα radiation. Crystal sizes were estimated from the broadening of the diffraction peaks using the Scherrer equation. *In situ* X-ray powder patterns were obtained as previously described.[10]

Surface areas were obtained from isotherms measured with a Quantachrome Autosorb using N₂ as adsorbant at 77 K.

Catalytic ammonia synthesis activities were recorded at pressures from 1 to 100 bar, temperatures between 320 and 500 °C, and in 3∶1 and 1∶1 H₂–N₂ gas mixtures using the set-up previously described.[11] The reported activities are based on the mass of catalyst loaded into the reactor and given as ml ammonia (at STP) produced per hour per gram of catalyst.

In order to conclusively establish that the ternary nitrides are stable under ammonia synthesis, an *in situ* XRPD experiment was conducted. A small amount of NH₅(CoOHMoO₄)₂ was loaded into a capillary reactor and transferred to the *in situ* XRPD set-up. A stream of pure ammonia was passed through the sample while it was heated at 0.5 °C min⁻¹ to 600 °C at ambient pressure. It was seen that the starting material, NH₅(CoOHMoO₄)₂ (prepared by precipitation from a cobalt nitrate and ammonium heptamolybdate solution kept at pH = 8 for 3 days) initially transformed into Co and MoO₂ at 470 °C and a little later MoO₂ transforms into γ-Mo₂N. Finally, Co₃Mo₃N is formed at 600 °C from Co and γ-Mo₂N. From this reaction sequence it was natural to attempt the preparation of Co₃Mo₃N by impregnation of γ-Mo₂N with a metal salt followed by ammonolysis. In principle, this method might be applicable for the preparation of a wide range of ternary or quarternary nitride materials. When formation of Co₃Mo₃N was confirmed in the *in situ* XRPD set-up the sample was cooled to 400 °C and the gas changed to a 3∶1 mixture of H₂–N₂ at 25 bar. No further changes in the X-ray powder pattern were observed and it was possible to detect formation of ammonia using a Baltzers quadrupole mass spectrometer connected to the exit stream from the capillary reactor.

Fig. 1 shows the X-ray powder pattern obtained at 400 °C, 25 bar in a 3∶1 mixture of dihydrogen and dinitrogen. All
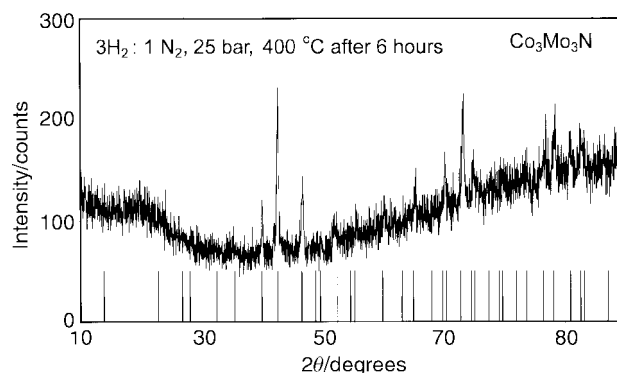

Fig. 1 *In situ* X-ray powder pattern obtained from Co₃Mo₃N at 400 °C, 25 bar in a 3∶1 mixture of dihydrogen and dinitrogen. Calculated positions of the diffraction lines for Co₃Mo₃N are also shown.

Table 1 Selected properties of molybdenum nitride and ternary nitride catalysts

Catalyst	Space group	BET surface area/m^2 g^{-1}	Average crystal size/nm
γ-Mo$_2$N	$Pm3m$	203	3.6
Fe$_3$Mo$_3$N	Fdm	8	45.0
Co$_3$Mo$_3$N	$Fd3m$	11	39.0
Ni$_2$Mo$_3$N	$P4_132$	7	44.0

diffraction lines are assigned to Co$_3$Mo$_3$N and it is concluded that Co$_3$Mo$_3$N is stable under ammonia synthesis conditions. *In situ* XRPD experiments were not conducted with Fe$_3$Mo$_3$N and Ni$_2$Mo$_3$N. However, no other compounds or phases were found using XRPD on spent catalyst samples.

Table 1 summarizes selected properties of the ternary nitrides prepared by ammonolysis of mixed oxide precursors. For comparison γ-Mo$_2$N is also included. It is seen that significantly lower surface areas are obtained for the ternary nitrides compared to that of γ-Mo$_2$N. The surface areas are in reasonable agreement with those estimated from the average crystal sizes. Promotion of the catalysts with *ca.* 5 wt% caesium did not result in a significant change in crystal size or surface area.

Catalytic activities were measured at 400 °C and 100 bar pressure. The inlet gas contained 4.5% ammonia in 3:1 dihydrogen–dinitrogen. The flow rate was adjusted to obtain 12% ammonia in the exit gas. Table 2 summarizes the activities of the unpromoted and caesium-promoted catalysts. It is observed that the activities are significantly enhanced by caesium promotion. For comparison the activity of a commercial multi-promoted iron catalyst, KM1,[12] is *ca.* 750 ml ammonia h^{-1} g^{-1} under similar conditions but at 410 °C.[13] Fig. 2 directly compares the activity of the caesium-promoted Co$_3$Mo$_3$N with that of the commercial catalyst at 400 °C and 50 bar in a 3:1 mixture of dihydrogen and dinitrogen. The feed flow was varied to study the influence of the exit concentration of ammonia on the activity. It is seen that both catalysts are inhibited by ammonia. Under these conditions the Cs/Co$_3$Mo$_3$N catalyst is significantly more active than the commercial iron catalyst. An activation energy of 54 kJ mol^{-1} was found for Cs/Co$_3$Mo$_3$N at constant conversion using the activity data at 50 bar and 320, 360, 400 and 440 °C. It should be noted that all activities reported here are based on the mass of catalyst. Industrially, the volume-based activities are usually more relevant and in this context it is important to note that the bulk

Table 2 Catalytic ammonia synthesis activities of molybdenum nitride and ternary nitride catalysts at 400 °C, 100 bar and *ca.* 8% ammonia

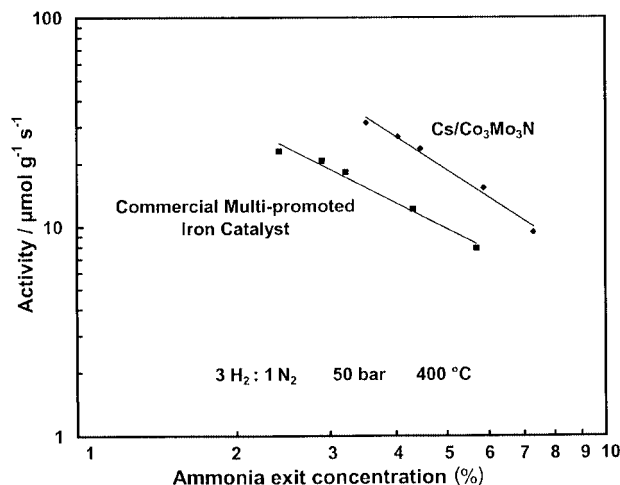| Catalyst	Ammonia production/ml h^{-1} g^{-1}
γ-Mo$_2$N	30
Fe$_3$Mo$_3$N	90
Co$_3$Mo$_3$N	120
Ni$_2$Mo$_3$N	80
Cs/Fe$_3$Mo$_3$N	440
Cs/Co$_3$Mo$_3$N	1040
Cs/Ni$_2$Mo$_3$N	530

Fig. 2 Catalytic activities of caesium-promoted Co$_3$Mo$_3$N and a commercial multi-promoted iron catalyst.

densities of the nitride catalysts are as high as those of iron based catalysts.

Previously, molybdenum nitride has been reported to exhibit high activity in catalytic ammonia synthesis.[14] However, it is seen that the activities of the ternary nitride catalysts are significantly higher. Particularly, the caesium promoted Co$_3$Mo$_3$N catalyst appears interesting. Since the ternary nitride catalysts are formed by ammonolysis at 600 °C they are expected to be very stable during the conditions of ammonia synthesis. The activity shown for Cs/Co$_3$Mo$_3$N was unchanged after two weeks at 400 °C and 50 bar. Possibly, other ternary nitrides will also be active ammonia synthesis catalysts.

Notes and references

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