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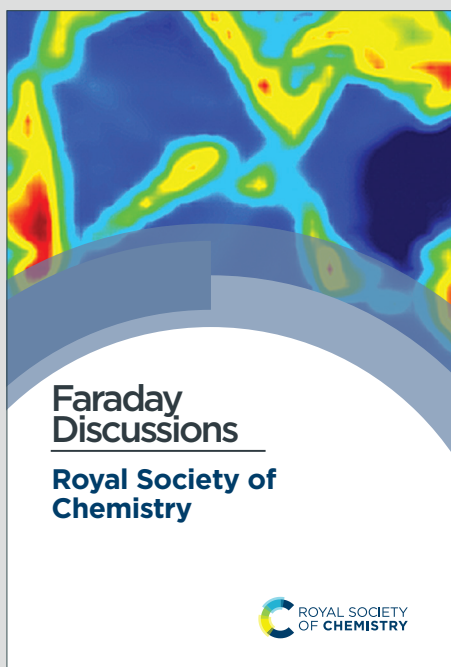
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The Role of H₂:N₂ Ratio on the NH₃ Synthesis Rate and on Process Economics over the Co₃Mo₃N Catalyst

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In this study, the process economics of ammonia synthesis over Co₃Mo₃N was investigated by searching an optimum feed stoichiometry. By ammonia synthesis rate measurements at atmospheric pressure and 400 °C over Co₃Mo₃N, it was found that, the rate was independent of H₂:N₂ stoichiometries above 0.5:1. For H₂:N₂ stoichiometries below 0.5:1, there was a linear dependency of ammonia synthesis rate on the H₂:N₂ stoichiometry. Static measurements of hydrogen adsorption isotherms measured at 25, 50, and 100 °C revealed that the adsorbed amounts of the strongly bound hydrogen over Co₃Mo₃N surface were saturated at around 100 Torr hydrogen pressure. This pressure corresponds to the partial pressure of hydrogen when H₂:N₂ stoichiometries are around 0.5:1, correlating the role of strong hydrogen in ammonia synthesis. These results were used to modify an existing kinetic expression to be used in a conceptual design, based on a lateness of mixing strategy for the hydrogen stream. This conceptual design and its economical analysis revealed that keeping low hydrogen stoichiometries can cut the investment and operating costs by a factor of 2.

Introduction

Ammonia production is one of the most energy intensive chemical processes. It consumes approximately 1-2% of the world energy production [1], [2]. One of the main operating costs that influences the price of ammonia is the cost of hydrogen. According to the analysis of U.S. Department of Energy in one of their reports, the proportional cost of H₂ for NH₃ is about 70% [3]. Moreover, according to an estimation from the International Energy Agency, 3% of CO₂ anthropogenic emissions is sourced from steam methane reforming which is currently a major route for the production of the H₂ feed for ammonia manufacture [4, 5].

It has been established that the catalytic ammonia synthesis reaction can be poisoned by hydrogen especially over supported Ru based catalysts [6-8]. This fact is represented in semi-empirically derived ammonia synthesis reaction rate expressions [9-11]. In order to improve ammonia synthesis rates, a number of studies such as operating the reactor under unsteady state conditions and decreasing the hydrogen partial pressure in the feed have been reported in the literature. In a number of cases, higher ammonia synthesis rates were reported in the literature with lower H₂:N₂ ratios than the stoichiometric ratio of 3:1 [12,13]. Unsteady state reactor operation has been suggested in the literature for ammonia synthesis over various types of ammonia synthesis catalysts [14–17]. Rate improvements have been achieved in all of the studies under cyclic operation conditions dependent upon the type of catalyst. Additional intensification strategies were also suggested: Cussler and co-workers have studied the effect of absorption of synthesized ammonia on an absorbent. Their studies showed that supported absorbents (e.g. MgCl₂ supported on zeolite-Y) can be used in a packed column instead of using a high-pressure condenser in order to separate ammonia [18–22].

Co₃Mo₃N catalysts are potentially promising for application as a nitrogen transfer reagents. It was known from the earlier studies that molybdenum nitrides possess activity for ammonia synthesis [24,25]. Kojima and Aika [23] used Co₃Mo₃N for ammonia synthesis and observed significant NH₃ synthesis rates at 300-400 °C and atmospheric pressure. Kojima and Aika also reported an ammonia synthesis rate expression over Co₃Mo₃N catalyst at 400 °C and 31 bar pressure based on power law kinetics [23].

$$r \left(\frac{\mu\text{mol}}{\text{gcat. s}} \right) = 10^3 \exp \left(-\frac{56 \frac{\text{kJ}}{\text{mol}}}{RT} \right) P_{\text{N}_2} P_{\text{H}_2}^{0.8} P_{\text{NH}_3}^{-1.34} \quad (1)$$

This rate expression reflects the positive dependency of the reaction rate on the reactants as well as the poisoning by the product. Hargreaves and co-workers showed while the catalytic ammonia synthesis reaction under flow of H₂:N₂ can be carried out over extended reaction times, in the presence of Ar:H₂ flow low levels of ammonia production were produced prior to an apparent phase change from Co₃Mo₃N to Co₆Mo₆N [26–28]. The regeneration of Co₆Mo₆N to Co₃Mo₃N under N₂ at 700 °C [28, 29] was also reported meaning that Co₃Mo₃N can be used as a N chemical looping reagent. Recently, Zeinalipour-Yazdi et al. modelled the mechanism of ammonia synthesis over Co₃Mo₃N using DFT calculations [30-32]. The results such calculations indicated that the

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ammonia synthesis reaction could proceed over $\text{Co}_3\text{Mo}_3\text{N}$ via a N based Mars-van Krevelen/associative mechanism [30]. Activated non-dissociated N_2 activated at nitrogen vacancy sites was proposed to be hydrogenated with gas and/or weakly bound hydrogen on the $\text{Co}_3\text{Mo}_3\text{N}$ surface [30]. DFT studies indicated that hydrogen can adsorb on Mo_3N sites molecularly and/or on Co_8 or N_{vacant} sites dissociatively [31]. On the other hand, there are very few experimental studies addressing the hydrogen adsorption/desorption characteristics over $\text{Co}_3\text{Mo}_3\text{N}$ catalysts in the literature. Therefore, it is of interest to investigate the activation of hydrogen by $\text{Co}_3\text{Mo}_3\text{N}$ surface in relation to its interesting ammonia synthesis performance. Additionally, in the current study, the possibility of operating the ammonia synthesis reaction over $\text{Co}_3\text{Mo}_3\text{N}$ at lower $\text{H}_2:\text{N}_2$ ratios has been investigated from the perspective of the economics of the ammonia production process. Hydrogen adsorption over $\text{Co}_3\text{Mo}_3\text{N}$ surface has been determined at different temperatures and additionally, steady state ammonia synthesis experiments have been performed at different $\text{H}_2:\text{N}_2$ ratios in the light of the H_2 adsorption experiments. The results of ammonia synthesis experiments at different $\text{H}_2:\text{N}_2$ ratios are evaluated in terms of the process economics.

Experimental

Synthesis of $\text{Co}_3\text{Mo}_3\text{N}$

The details of synthesis procedure for $\text{Co}_3\text{Mo}_3\text{N}$ catalyst can be found elsewhere [28]. Briefly, 5.59 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, $\geq 98\%$ purity) and 4 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich, 81-83% as MoO_3) were used. The metal salts were dissolved in 200 ml deionized water and heated to 80 °C over a magnetic stirrer in a fume cupboard. The indication of the starting of the reaction between metal salts was a colour change at ca. 80 °C at which point the colour of the aqueous solution changed from red to purple. After the colour change occurred, stirring was carried out for a further 1 h. Then, the solution was filtered and the filtered material was washed twice with water and ethanol. The filter cake was dried overnight at room temperature and the purple powder was placed on a watch-glass and further dried in an oven at 150 °C overnight. After the drying process was completed, the cobalt-molybdenum containing precursor was calcined in a tube furnace in air at 500 °C for 3 hours (applying a temperature ramp rate of 20 °C min^{-1}). After calcination, the cobalt-molybdenum oxide powder was placed into an ammonolysis reactor and for nitridation using a flow of 50 ml min^{-1} ammonia. The temperature programme of the furnace applied during ammonolysis was as follows: (i) ambient temperature to 357 °C at a rate of 5.6 °C min^{-1} , (ii) from 357 °C to 447 °C at a rate of 0.2 °C min^{-1} and (iii) from 447 °C to 785 °C at a rate of 2.1 °C min^{-1} . The temperature of the furnace kept constant at 785 °C for 5 hours then cooled to room temperature under ammonia flow. At the end of the ammonolysis process, catalyst was flushed with N_2 and exposed to 2% O_2 in Ar flow (10 ml/min) further diluted with N_2 for passivation. After passivation, amorphous $\text{Co}_3\text{Mo}_3\text{N}$ powder was synthesized. In order obtain crystalline $\text{Co}_3\text{Mo}_3\text{N}$ material, the powder was treated at 700 °C (temperature ramp: 10 °C/ min) for 3 h in the presence of $\text{H}_2:\text{N}_2=3:1$ flow at 60 ml/min . The catalyst in powder form was sieved with the sieves having ASTM standards and with openings of 125 μm , 106 μm , 38 μm and a collecting pan. A sieve shaker (Retsch, AS200) was used for 30 min to sieve the catalyst.

Characterization

X-Ray Diffraction (XRD)

Powder diffraction analyses were performed using a Siemens D5000 instrument operating with a $\text{Cu K}\alpha$ X-ray source. A 2θ range between 5° and 85° was scanned using a counting rate of 1 second per step with a step size of 0.02°.

CHN Elemental Analysis

Elemental analysis of $\text{Co}_3\text{Mo}_3\text{N}$ was carried out using an Exeter Analytical CE-440 elemental analyser.

Temperature Programmed Reduction

Temperature programmed reduction (TPR) analysis was performed in a Micromeritics Chemisorb 2720 instrument. The sample holder of the instrument containing pre-weighed $\text{Co}_3\text{Mo}_3\text{N}$ sample was connected to the manifold and temperature programmed reduction (TPR) was carried out under a 25 ml/min flow of 10% H_2 in Ar (Linde) gas with a temperature ramp of 10 °C/ min up to 900 °C.

H_2 -Chemisorption

Hydrogen chemisorption experiments were performed in a home-built high-vacuum glass manifold equipped with a MKS Baratron gauge (up to 1000 Torr pressure), high vacuum Teflon valves (ACE Glass) and a vacuum pump (Pfeiffer, up to 10^{-6} Torr). The general characteristics of the experimental set up and the measurements have been described in detail elsewhere [33]. Briefly, the sample chamber was connected to the manifold. Temperature was increased with a rate of 4 °C/ min and kept constant at 500 °C during the reduction process. A known pressure of hydrogen gas between 50 Torr and 600 Torr was admitted to the catalyst. After 30 min treatment, the manifold was evacuated for 10 min. The same procedure was then repeated 4-5 times in order to be sure that the surface of the $\text{Co}_3\text{Mo}_3\text{N}$ catalyst was reduced completely. After reduction of $\text{Co}_3\text{Mo}_3\text{N}$, the manifold was evacuated for 3 hours

at 500 °C. H₂ adsorption isotherms were obtained at 25 °C, 50 °C and 100 °C. The measurements were performed between 1 and 600 Torr hydrogen pressure. After each hydrogen dose, the catalyst was exposed to hydrogen gas for 10 min which was found to be sufficient in terms of thermal and chemical equilibration.

Kinetic Studies

Ammonia synthesis experiments were carried out at 400 °C, under atmospheric pressure and 100 ml min⁻¹ gas flow with N₂ (99.999%, Linde) and H₂ (99.999%, Linde) gases. The H₂:N₂ ratio was changed between 0.05 and 3.0 by regulating the N₂ and H₂ gas flow rates while the total flow rate was kept constant at 100 ml min⁻¹. The flow rates were adjusted by mass flow controllers (MKS) driven by a control station (Terralab). The 6.0 mm OD reactor was heated in a temperature controlled tube furnace. 150 mg of Co₃Mo₃N catalyst with a particle diameter between 38 and 106 μm was loaded into the reactor. Prior to the activity measurements, the catalyst was treated under 100 ml min⁻¹ H₂:N₂ (3:1) flow at 700 °C for 2 hours. After the pre-treatment, the catalyst was cooled to 400 °C. The effluent gases during ammonia synthesis experiments were sent to a wash bottle containing a 0.00108 M H₂SO₄ solution. The reaction rate of ammonia synthesis was determined following the change of conductivity of the H₂SO₄ solution as a function of time. The conductivity change of the H₂SO₄ solution was determined with a conductivity meter (Jenway, 4020 model). The conductivity change of H₂SO₄ solution occurs due to the neutralization reaction between H₂SO₄ and NH₃. The amount of produced ammonia is determined by using a conversion factor which is calculated from the linear relationship between the conductivity of 0.00108 M of H₂SO₄ and 0.00108 M (NH₄)₂H₂SO₄ solutions as 0.583 μmol NH₃/(μS*cm⁻¹). Following the kinetic measurements, samples were purged under 100 ml min⁻¹ pure Ar (99.999%, Linde) flow to monitor total amount of NH₃ adsorbed on the catalysts.

CHEMCAD Simulations

CHEMCAD simulation is performed in order to show the effect of using a lower H₂:N₂ on both investment and operating costs of the process. An ammonia synthesis loop was devised that consists of a packed bed reactor, a flash column, a compressor and some auxiliary units. Ammonia synthesis reactor was operated isothermally at 673 K and under 100 bar pressure with different H₂:N₂ ratios (H₂:N₂=3:1 and H₂:N₂=1:1). Kinetics were based on Kojima and Aika [23] given in equation (1) was used in the simulation. All of the produced ammonia was obtained in a pure form using the flash drum. The unreacted H₂ and N₂ was recycled to the ammonia synthesis reactor. The compressor was operated adiabatically.

During the simulation, a fresh feed of 100 kmol/h is fed to the loop. Two different feed ratios are used in the simulation which are H₂:N₂ =3:1 and 1:1. The amount of produced ammonia was kept constant by changing the volume of the reactor during the simulations of different feed ratios. As a result, the reactor volumes, the compressor duties, and the compressor capacities could be compared on the same basis of ammonia production.

Results and discussion

Characterization

XRD and Elemental Analysis

The XRD pattern of the Co₃Mo₃N material is presented in Figure 1. The marked reflections are consistent with previous reports for the Co₃Mo₃N phase [27,34]. In addition, the high background of the pattern can be attributed to contribution of fluorescence of the Co containing sample being investigated with a Cu based X-ray source.

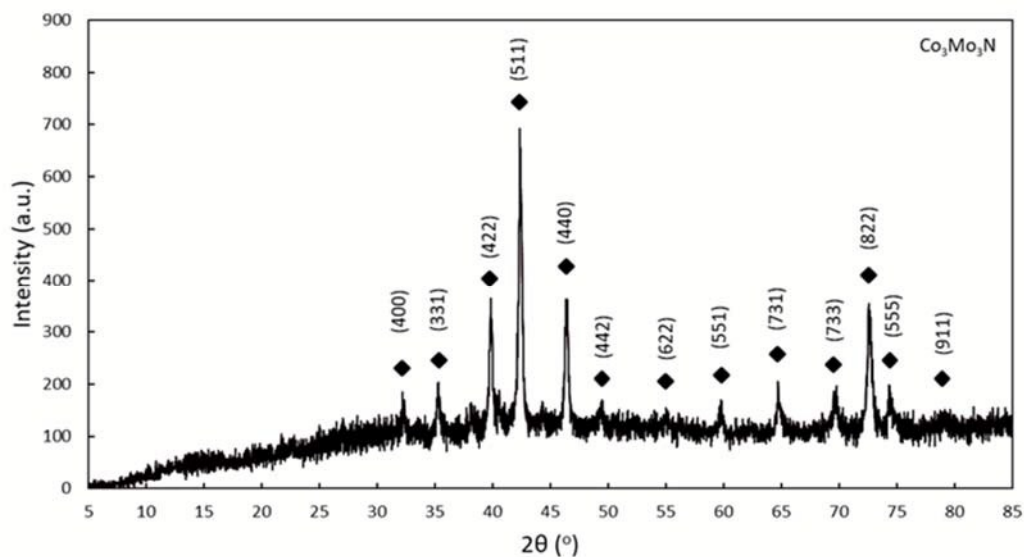


Figure 1. XRD Pattern of $\text{Co}_3\text{Mo}_3\text{N}$ (the peaks marked with a diamond belong to $\text{Co}_3\text{Mo}_3\text{N}$)

The nitrogen content of the $\text{Co}_3\text{Mo}_3\text{N}$ material was determined using CHN analysis. The average result of two experiments is shown in Table 1 demonstrating there to be reasonable agreement between the experimentally measured amount of nitrogen and that expected on the basis of stoichiometric considerations which is also consistent with the literature [26,31].

Table 1. Elemental analysis results (nitrogen content) of synthesized $\text{Co}_3\text{Mo}_3\text{N}$

Material	Nitrogen content ^a , wt%	Nitrogen content ^b , wt%
$\text{Co}_3\text{Mo}_3\text{N}$	2.93	2.70

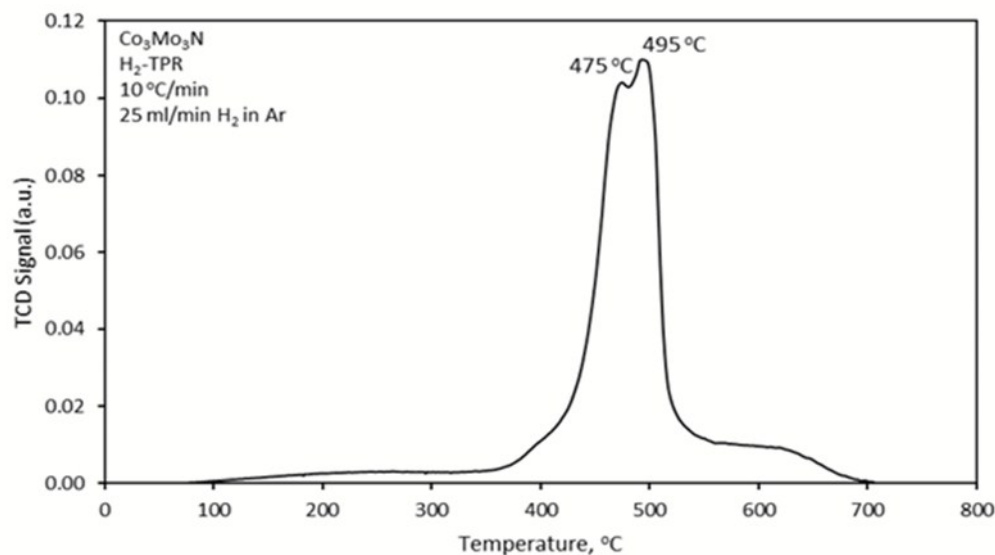
^a Theoretical
^b Experimental

Temperature Programmed Reduction

The H_2 -TPR profile of the $\text{Co}_3\text{Mo}_3\text{N}$ material is given in Figure 2 corresponding to 25 ml/min of H_2 in Ar (10 % H_2 in Ar) with a temperature ramp rate of 10 °C/min. Two peaks centred at 475 °C and 495 °C, respectively can be observed. In addition, there is a significant background during TPR analysis that starts at 100 °C, a shoulder at 400 °C and the TCD signal does not return to its baseline until ca. 700 °C. The hydrogen consumption was calculated as 3.0×10^{-3} mol H_2 $\text{g}_{\text{catalyst}}^{-1}$ with quantification being based on the calibration experiment of Ag_2O reduction.

The surface of $\text{Co}_3\text{Mo}_3\text{N}$ catalyst was passivated with dilute oxygen as a part of the preparation procedure. The possible oxide structures on the oxidized surface can be possibly considered to be CoO , MoO_3 , and CoMoO_4 . The consumed amount of hydrogen can be compared with the amount of oxygen sites and/or oxide layer on the surface of the oxides to determine which type of oxide could be dominant on the $\text{Co}_3\text{Mo}_3\text{N}$ surface before reduction. Hargreaves and co-workers demonstrated that the structure of $\text{Co}_3\text{Mo}_3\text{N}$ changed to $\text{Co}_6\text{Mo}_6\text{N}$ under H_2 :Ar flow at 700 °C [26-28]. Therefore, some part of the H_2 consumption could be related to hydrogenation of nitrogen from the structure of $\text{Co}_3\text{Mo}_3\text{N}$. The remaining part of the H_2 consumption (during H_2 -TPR analysis) is considered to be used for the reduction of surface oxygen atoms and/or oxide layers.

The surface oxygen atoms of possible oxides are determined as shown in Table 2 by taking into consideration their crystal structures. After that, the required amount of H_2 to reduce surface oxygen atoms are calculated and it is found out that the amount of H_2 consumption (during TPR analysis) is two orders of magnitude higher than the required H_2 amount (given in Table 2), which means that material balance in terms of H_2 consumption is still open. In this situation, an additional analysis is carried out by assuming if an oxide layer (having a thickness) is formed during the passivation process over $\text{Co}_3\text{Mo}_3\text{N}$. The calculations were performed using the number of oxygen atoms in a unit cell of each possible oxides as given in Table 3. As a result of the calculations, the thicknesses of oxide layers of CoO , MoO_3 , and CoMoO_4 were determined as 5.1, 3.6, and 4.6 nm, respectively.

Figure 2. H₂-TPR pattern of Co₃Mo₃NTable 2. Comparison of required amount of H₂ to reduce the possible oxides on passivated Co₃Mo₃N surface

Oxide type	^a Amount of oxygen sites, O sites cm ⁻²	Required amount of H ₂ , mol H ₂ g _{catalyst} ⁻¹
CoO	0.55x10 ¹⁵	1.8x10 ⁻⁵
MoO ₃	1.70x10 ¹⁵ (Plane 1)	0.6x10 ⁻⁵
	0.58x10 ¹⁵ (Plane 2)	1.9x10 ⁻⁵
CoMoO ₄	0.54x10 ¹⁵ (Plane 1)	1.8x10 ⁻⁵
	0.48x10 ¹⁵ (Plane 2)	1.6x10 ⁻⁵

^a The amount of oxygen sites per cm² is calculated using the crystal structures of the oxides

Table 3. Corresponding oxide layer thicknesses calculated using consumed amount of H₂ during H₂-TPR analysis

Oxide type	Number of O atoms in a unit cell	Thickness of oxide layer, nm
CoO	4	5.1
MoO ₃	26	3.6
CoMoO ₄	32	4.6

The H₂-TPR behaviour is consistent with the reports in the literature: two peaks are observed during the reduction of cobalt oxides around at ca. 300 °C (Co₃O₄ to CoO) and 400 - 500 °C (CoO to Co) [36-38]. Similarly two peaks are reported concerning the reduction of MoO₃ to Mo which the low and high temperature peaks occur between 730-770 (MoO₃ to MoO₂) and 850 - 1000 °C (MoO₂ to Mo), respectively [39,40]. The reported high temperature range for the reduction of MoO₂ to Mo may be related to the experimental conditions applied. In terms of the reduction behaviour of CoMoO₄, different reduction temperatures are reported. In the first case, the reduction peak of CoMoO₄ occurs at ca. 550 – 600 °C [41] (20 °C min⁻¹, 15% H₂ in N₂). In the second case, the reduction temperature of CoMoO₄ is given as 715 °C [42] (10 °C min⁻¹, 5% H₂ in Ar). In the light of material balance calculations and the reduction peak positions that are reported in the literature, all of the oxide phases could be present on the catalyst surface. From a more practical perspective, the low temperature reduction peaks that are obtained in this study (low intensity broad peak at around 250 °C and the shoulder at 400 °C) are identified with the reduction peaks of Co₃O₄ and that of CoO that are reported in the literature. The intensity of these two features are determined as 3x10⁻⁴ mol/g catalyst. When this hydrogen consumption amount is attributed to a monolayer coverage of oxygen on the surface with the rule of thumb of 10¹⁵ surface atoms of oxygen/g catalyst, corresponding to a typical surface site density of similar oxides, a surface area was estimated as 6.6 m²/g, which is in the same orders of magnitude with the BET surface area, measured as 2 m²/g. The surface area calculated from H₂ TPR is obtained after peak-fitting, which is prone to errors especially when subtracting the long tailing peaks. Furthermore, caution must be exercised with our assumption of CoO reduction which consumes a different amount of hydrogen than CoOx with a different

oxygen stoichiometry. Hence, we conjure that we can regenerate the surface by reduction at around 400 °C without altering the rest of the structure too much.

H₂ adsorption isotherms

The H₂ adsorption isotherms of Co₃Mo₃N catalyst at 25 °C, 50 °C and 100 °C, which are given in Figure 3, show that the amount of H₂ adsorption decreases with increasing temperature, consistent with the exothermic spontaneous adsorption of hydrogen over these surfaces. Additionally, it is observed that after 100 Torr H₂ pressure, H₂ adsorption behaviour over Co₃Mo₃N surface changes with a plateau being observed. This plateau is interpreted as the saturation of the catalyst surface with monolayer of adsorbed hydrogen. In fact, if the saturation coverage of 30 μmol H₂/gram catalyst, i.e., 60 μmol H/gram-catalyst is converted to corresponding number of sites that are available, it can be found that 2.4 × 10¹⁹ sites/g catalyst is calculated. If, again, we use the rule of thumb of 10¹⁵ sites/cm², a surface area estimation of 2.4 m²/g catalyst is obtained, which is consistent with the BET value given in Table 5. Further discussion of this and alternative methods of surface area calculations will also be presented later. As a result, it is fair to conclude that the monolayer hydrogen coverage of this catalyst occur around 100 Torr and it is about 30 μmol H₂/gram catalyst. In the later section we will relate this coverage to the hydrogen partial pressures used during the reactions in this study.

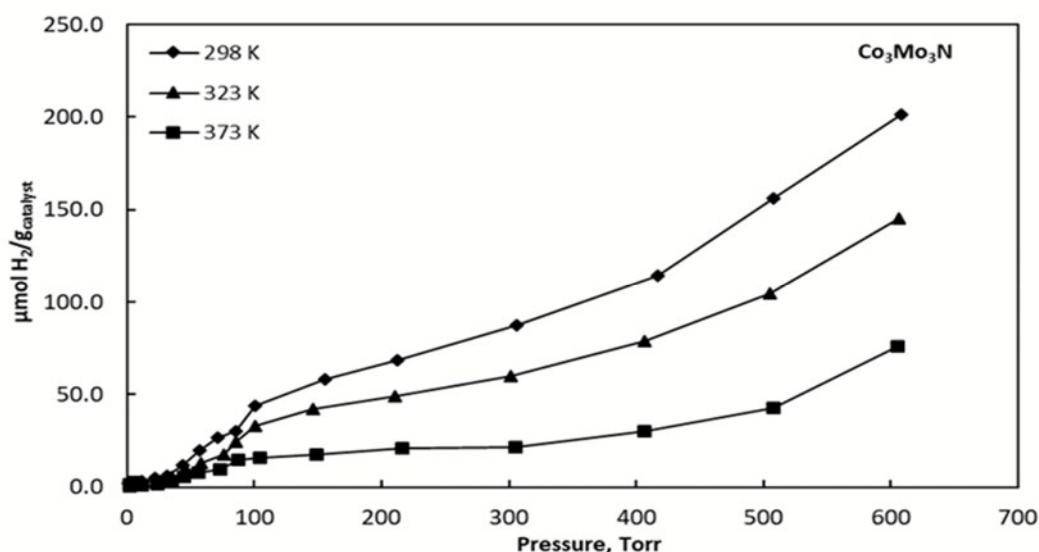


Figure 3. H₂ adsorption isotherms of Co₃Mo₃N at 25 °C, 50 °C, and 100 °C

Kinetic Studies

NH₃ synthesis experiments under steady state flow

Ammonia synthesis rates measured between 400 – 475 °C and under atmospheric pressure were given in Table 4. The apparent activation energy calculated from the kinetic data was also given in Table 4. The reported ammonia synthesis rate over Co₃Mo₃N in the literature was 165 μmol g⁻¹ h⁻¹ at 400 °C [43]. The ammonia synthesis rate was measured as 115 μmol g⁻¹ h⁻¹ at 400 °C and under atmospheric pressure. In Table 5, the comparison of ammonia synthesis rates of Co₃Mo₃N catalysts and their BET surface area are given. It must be noted that, the surface area of Co₃Mo₃N catalyst was determined with three different methods: H₂-chemisorption, H₂-TPR and N₂ adsorption at 77 K (the classical BET method). The BET surface area of the catalyst is measured as 2.0 m²/g. The chemisorption related calculations revealed 2.4 m²/g for dissociative adsorption and 1.7 m²/g for molecular adsorption of H₂. The TPR measurements revealed a surface area in the vicinity of 6.6 m²/g with the assumption of the reduction of a monolayer of CoO. The three of the different surface area calculations are obtained in the same order of magnitude (lower than 10 m²/g) and is in agreement with literature [35,49].

In the light of data presented in Table 5, the very slightly lower rate measured is possibly related to the different textural properties of the catalyst tested in this study. The apparent activation energy was determined to be 90 kJ/mol using an Arrhenius plot, and is in general agreement with the literature [10,44,45]. It should be noted that the apparent activation energy was calculated under

conditions where the ammonia synthesis reaction was far away from equilibrium. On the other hand, Kojima and Aika reported an apparent activation energy of 56.5 kJ/mol between 315 – 400 °C and under 31 bar pressure over $\text{Co}_3\text{Mo}_3\text{N}$ [23].

Table 4. Measured ammonia synthesis rates and calculated apparent activation energy over $\text{Co}_3\text{Mo}_3\text{N}$

Temperature, °C	NH_3 Synthesis Rate, $\mu\text{mol g}^{-1} \text{h}^{-1}$	Apparent Activation Energy, kJ/mol
400	115	90
425	182	
450	330	
475	571	

Table 5. Comparison of ammonia synthesis activity with respect to surface area of $\text{Co}_3\text{Mo}_3\text{N}$ catalyst

Reference	Surface Area, $\text{m}^2 \text{g}^{-1}$	NH_3 Synthesis Rate, $\mu\text{mol g}^{-1} \text{h}^{-1}$
This work	2	115
[43]	18	165

NH_3 synthesis experiments at different $\text{H}_2:\text{N}_2$ ratios

Ammonia synthesis rate measurements were performed with different $\text{H}_2:\text{N}_2$ ratios under a steady flow of 100 ml/min at 400 °C and atmospheric pressure in a differential packed bed reactor. The average values of ammonia synthesis rate in each data point are reported in Figure 4 with error bars determined for 95% confidence interval. No significant change is observed with the change of $\text{H}_2:\text{N}_2$ ratio on the ammonia synthesis rate when the $\text{H}_2:\text{N}_2$ ratio is greater than 0.5. The corresponding partial hydrogen pressures between $\text{H}_2:\text{N}_2=3.0$ and $\text{H}_2:\text{N}_2=0.5$ are 570 and 253 Torr, respectively. In contrast, the ammonia synthesis rate increases with increasing $\text{H}_2:\text{N}_2$ ratio at ratios when $0 < \text{H}_2:\text{N}_2 < 0.5$. When the decrease in the ammonia synthesis rate at lower $\text{H}_2:\text{N}_2$ ratios ($\text{H}_2:\text{N}_2 < 0.5$) and the hydrogen adsorption behaviour over $\text{Co}_3\text{Mo}_3\text{N}$ at lower hydrogen pressures ($P_{\text{H}_2} < 100$ Torr) are compared (Figure 4), a direct relationship between the amount of adsorbed hydrogen on $\text{Co}_3\text{Mo}_3\text{N}$ surface and the ammonia formation rate can be observed. Therefore, it can be inferred that the monolayer adsorbed hydrogen is the reactive form for $\text{Co}_3\text{Mo}_3\text{N}$ catalyst in ammonia synthesis.

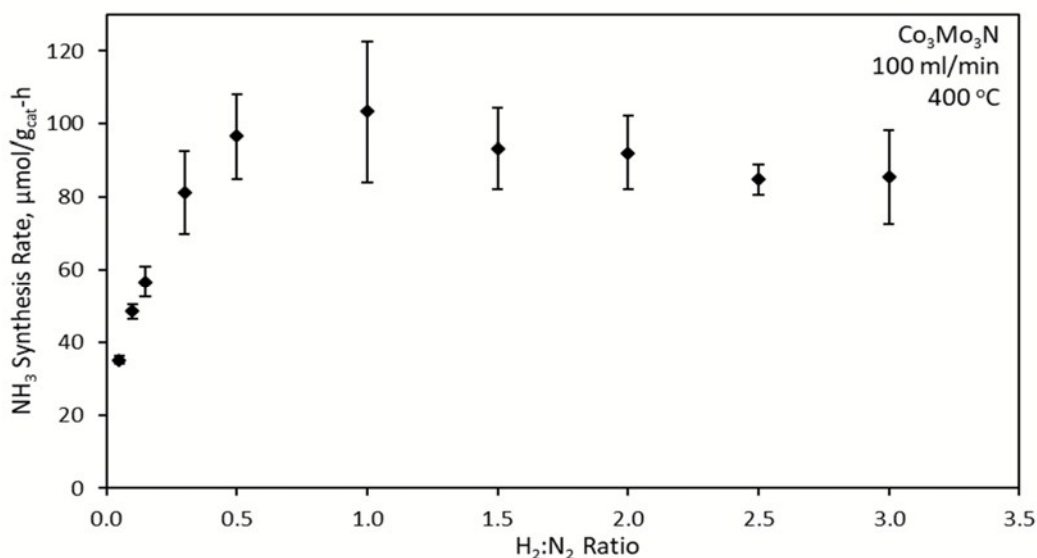


Figure 4. Effect of $\text{H}_2:\text{N}_2$ ratio on the ammonia synthesis rate over $\text{Co}_3\text{Mo}_3\text{N}$ catalyst at 400 °C

The reason for the change of H_2 adsorption behaviour over $\text{Co}_3\text{Mo}_3\text{N}$ and the independence of ammonia synthesis rate of $\text{H}_2:\text{N}_2$ ratio when the $\text{H}_2:\text{N}_2$ ratio is larger than 0.5 can also be explained comparing the surface coverage of H_2 at 100 Torr pressure at 25 °C and BET surface area of the $\text{Co}_3\text{Mo}_3\text{N}$ material. The kinetic diameter of a H_2 molecule is reported as 0.289 nm [46]. The surface area of $\text{Co}_3\text{Mo}_3\text{N}$ using the amount of hydrogen adsorption at 25 °C and 100 Torr (Figure 3) can be calculated as $1.7 \text{ m}^2 \text{g}^{-1}$. If the

same analysis is made using the diameter of a hydrogen atom taking into consideration of hydrogen dissociation over $\text{Co}_3\text{Mo}_3\text{N}$ (the van der Waals radius of the hydrogen atom is reported to be 0.12 nm [47]), the surface area of $\text{Co}_3\text{Mo}_3\text{N}$ would be determined as $2.4 \text{ m}^2 \text{ g}^{-1}$. As a result, the calculated surface area values of $\text{Co}_3\text{Mo}_3\text{N}$ are in close agreement with BET surface area, which is $2 \text{ m}^2 \text{ g}^{-1}$.

At this point, we will take the stride of correlating the monolayer coverages measured during chemisorption at $100 \text{ }^\circ\text{C}$ and the kinetic performances measured at $400 \text{ }^\circ\text{C}$. At atmospheric pressure, $0.5 \text{ H}_2:\text{N}_2$ stoichiometry correspond to H_2 partial pressure of around 250 Torr. Below this pressure, the reaction rate follows a linear dependency on hydrogen partial pressure. Hydrogen coverages measured by static isotherms indicate that the coverage of hydrogen also exhibit almost a linear relationship, albeit at $100 \text{ }^\circ\text{C}$. In other words, under the reaction conditions of $400 \text{ }^\circ\text{C}$, 250 Torr could be sufficient to provide the monolayer hydrogen coverage needed for chemical conversion. Any increase of hydrogen pressure does not increase hydrogen coverage on the surface, and hence the rates remain uninfluenced. It is demonstrated that lower H_2 partial pressures of H_2 (up to a limit which is $\text{H}_2:\text{N}_2 > 0.5$) is sufficient for carrying out the ammonia synthesis reaction with a similar rate compared to stoichiometric H_2 partial pressure over the $\text{Co}_3\text{Mo}_3\text{N}$ catalyst under atmospheric pressure and low conversion conditions. It was found that when the $\text{H}_2:\text{N}_2$ ratio equals to 0.5, a sufficient amount of hydrogen exists over the catalyst for covering the catalyst surface, which is the reactive form, according to H_2 chemisorption experiments and surface area calculations. When the $\text{H}_2:\text{N}_2$ ratio is lower than 0.5, the ammonia synthesis decreases due to the decrease in the surface coverage of hydrogen. As a result, the hydrogen coverage is an important parameter for ammonia synthesis reaction over $\text{Co}_3\text{Mo}_3\text{N}$ catalyst and monolayer coverage of hydrogen over the catalyst surface is the optimum value according to kinetic studies at $400 \text{ }^\circ\text{C}$ and different $\text{H}_2:\text{N}_2$ ratios under atmospheric pressure.

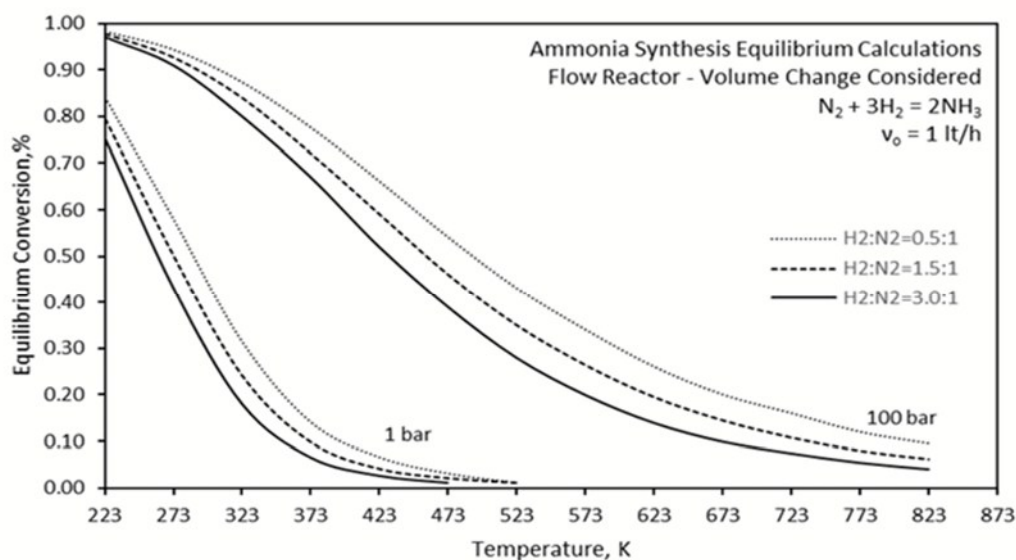


Figure 5. Equilibrium Conversion of NH_3 Synthesis Reaction at Different $\text{H}_2:\text{N}_2$ Ratios and Pressures

The stoichiometry can be changed under steady state conditions as was described above. It is also possible to change the stoichiometry by providing pure N_2 pulses, between excursions of stoichiometric operations. A time averaged stoichiometry will also be lower under such operations. Preliminary studies have also been undertaken on the application of interrupted flow regimes on the ammonia synthesis performance of the $\text{Co}_3\text{Mo}_3\text{N}$ catalyst and the initial results suggest that there is no advantage to operation under this regime. The end of experiment ammonia accumulation measured over the catalysts did not indicate substantial amounts of ammonia accumulating on the catalyst, as a result.

The possibility of using a lower amount of hydrogen with respect to stoichiometric ratio ($\text{H}_2:\text{N}_2=3:1$) over $\text{Co}_3\text{Mo}_3\text{N}$ catalysts can offer lower manufacturing costs. The thermodynamics of the ammonia synthesis reaction also favours the use of lower $\text{H}_2:\text{N}_2$ ratios under same operating pressures and temperatures as shown in Figure 5. The use of lower $\text{H}_2:\text{N}_2$ ratios influence the cost of the ammonia synthesis loop. When lower $\text{H}_2:\text{N}_2$ ratios are used, the flow rate of the recycle stream decreases due to the low amounts of hydrogen circulating in the reactor. Furthermore, lower flow rates with inherently small per pass conversions can afford smaller reactor volumes and smaller compressor capacities. This directly influences the compressor duty and decreases the operational and fixed cost of the ammonia synthesis loop. Therefore, an improvement can be achieved on the cost of ammonia manufacturing

with the help using lower amounts of hydrogen in the presence of $\text{Co}_3\text{Mo}_3\text{N}$ catalysts. In order to justify this logic, a conceptual design and economic analysis was performed using CHEMCAD.

Table 6. Comparison between the stoichiometric ($\text{H}_2:\text{N}_2=3:1$) and sub-stoichiometric ($\text{H}_2:\text{N}_2=1:1$) hydrogen feedings on the process economics for the same amount of produced ammonia amounts.

$\text{H}_2:\text{N}_2$	Fresh N_2 Feed, kmol/h	NH_3 Produced, kmol/h	Compressor Capacity, m^3/h (STP)	Compressor Duty, kW	Reactor Volume, m^3
3:1	30	5.2	12551	764.9	0.045
1:1	30	5.3	6131	382.2	0.033

The conceptual design procedure was aimed at determining the volume of the reactor, the recycle amounts, the compressor capacity and the cost of electricity needed for compression, for the same amount of ammonia produced using a stoichiometric feed $\text{H}_2:\text{N}_2=3.0$ and a feed that maintains stoichiometries in the vicinity of $\text{H}_2:\text{N}_2=0.5$. The ammonia synthesis reactor is operated isothermally at 673 K and under 100 bar pressure. The rate reported by Aika et al. [23], given in equation 1 was used which is consistent with the experimental evidence we collected under steady state and pulsed reactor operation conditions. The conceptual design is carried out under the conditions that the rate is independent of hydrogen partial pressure with a stoichiometry of 1. Additional hydrogen was provided along the progress of the reaction, under the conditions that can be represented as the lateness of mixing model of reactors [48].

On this catalyst, the effect of pulsed operation was also investigated. Pulses of pure nitrogen were sent during the reaction running under both stoichiometric or substoichiometric feed mixtures. The influence of a pulsing operation was not significant within the experimental conditions used in this study. The primary influence of pulsing with nitrogen should be to remove ammonia that is covering the surface and poisoning the reaction, also that can be deduced from equation 1. However, under our selected operating conditions, it was observed that the ammonia accumulation amounts were measured to be insignificant. Since the amount of the surface bound hydrogen was low, nitrogen pulsing did not also have any influence on removing the hydrogen poisoning effect. Finally, since the conversion levels were kept low, there was not a significant influence of nitrogen pulsing for replacing the lattice nitrogen to regenerate the catalyst. In fact, by keeping hydrogen partial pressures low under substoichiometric feeds, the process parameters, coupled to the surface and bulk processes of the catalyst, allowed the regeneration to take place under the steady state reaction conditions.

Conclusions

Ammonia synthesis was carried out over a $\text{Co}_3\text{Mo}_3\text{N}$ catalyst under steady and pulse flow conditions at atmospheric pressure and 400 °C and above and the apparent activation energy was determined to be 90 kJ/mol. H_2 -chemisorption experiments at various temperatures revealed that the $\text{Co}_3\text{Mo}_3\text{N}$ surface was saturated with strongly bound hydrogen at 100 Torr H_2 pressure. When the $\text{H}_2:\text{N}_2$ ratio was higher than 0.5, changing $\text{H}_2:\text{N}_2$ ratio did not influence ammonia synthesis rates under steady flow conditions. H_2 -chemisorption and reaction tests under steady flow conditions indicated that strongly bound hydrogen over $\text{Co}_3\text{Mo}_3\text{N}$ was the reactive form for ammonia synthesis. Using the implications of these results, the possibility of carrying out ammonia synthesis reaction with lower amount of hydrogen compared to stoichiometric ratio, an economic analysis was conducted. The results of economic analysis revealed that both the reactor volume and needed compressor capacity to recycle unreacted gases decreased by a factor of 2, hence decreasing the fixed costs. Furthermore, the operating costs of recycle gas compression decreased by a factor of 2 by decreasing the feed stoichiometry from 3:1 to less than 1:1. These comparisons revealed the benefits of lateness of mixing strategy on ammonia synthesis using $\text{Co}_3\text{Mo}_3\text{N}$ catalyst.

Conflicts of interest

There are no conflicts to declare.

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