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2 **Enhancing ammonia catalytic production over spatially**
3 **confined cobalt molybdenum nitride nanoparticles in SBA-15**
4

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1 **Abstract**

2 Ternary $\text{Co}_3\text{Mo}_3\text{N}$ nitrides are reported to exhibit high catalytic activity in ammonia synthesis.
3 However, synthesis of ternary nitrides requires thermal treatments at elevated temperatures and
4 reactive atmospheres that lead to unavoidable surface reduction ($\sim 10 \text{ m}^2 \text{ g}^{-1}$). In this work, we have
5 developed a novel approach to improve the catalytic activity of $\text{Co}_3\text{Mo}_3\text{N}$ through its dispersion
6 into a high surface area silica-based support (SBA-15). During ammonolysis and ammonia
7 synthesis conditions reaction, SBA-15 demonstrated good thermal and chemical stability
8 maintaining an ordered porous structure and high surface area ($> 500 \text{ m}^2 \text{ g}^{-1}$). For application in
9 ammonia synthesis, SBA-15 supported cobalt molybdenum catalysts with different metal loading
10 (10, 20 and 30 wt.%) were prepared by a modified impregnation-infiltration protocol and their
11 catalytic activity studied. The dispersion of CoMo nitride nanoparticles into SBA-15 structures
12 resulted in the improvement of their structural and textural properties of nitrides as evidenced by
13 XRD analysis, STEM-EDS, and N_2 - physisorption (*e.g.* 10-CoMo-N/SBA-15: $348 \text{ m}^2 \text{ g}^{-1}$).
14 Nevertheless, the surface composition of CoMo-N/SBA-15 catalysts was found to be similar to the
15 non-supported $\text{Co}_3\text{Mo}_3\text{N}$. Furthermore, supported CoMo-N/SBA-15 displayed enhanced catalytic
16 activity in ammonia synthesis ($1714, 1429$ and $810 \mu\text{mol g}_{\text{active phase}}^{-1} \text{ h}^{-1}$ corresponding to the CoMo
17 oxide loadings of 10, 20, 30 wt.% respectively) that outperform the classical $\text{Co}_3\text{Mo}_3\text{N}$ catalyst
18 ($298 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$). The results reported in this work highlights a novel approach for the design
19 of nitride-based catalysts with superior catalytic properties in ammonia synthesis.

20 **Keywords:** Ammonia synthesis, nitrides, confined nanoparticles, SBA-15

21

1 **1. Introduction**

2 To compensate the natural variation of power derived from natural resources, the development of
3 smart grid capable of cooperative electricity generation (mix of energy resources) and offering a
4 range of energy storage possibilities (short-, mid- and long- term energy storage) is of high
5 importance for large-scale renewable energy production. Among the energy storage systems,
6 Power to X (P2X) is expected to play a major role in long-term, large scale energy storage (days
7 to months). Within the multiples candidates for P2X, ammonia possesses suitable characteristics
8 to be considered as green, safe and sustainable energy carrier such as high hydrogen gravimetric
9 content (17.6 wt.%), high energy density (5.2 kWh kg⁻¹) based on the low heat value (LHV), facile
10 liquefaction and low flammability [1]. More importantly, there is an existing infrastructure for the
11 safe and cost-effective ammonia transportation and distribution worldwide which alas is not the
12 case for hydrogen [2].

13 The implementation of large-scale power to green ammonia, in the energy landscape is limited by
14 the development of novel and efficient processes for cost-effective green ammonia production.
15 Currently, large-scale ammonia production is achieved through the industrial Haber-Bosch process
16 (H-B) in which highly purified N₂ and H₂ react over a promoted iron-based catalyst under high
17 pressure (up to 200 bar) and temperature varying between 400 and 500 °C [3, 4]. While it sustains
18 a significant proportion of the global population through providing affordable nitrogen-based
19 fertilizers, the process is highly energy demanding. The H-B process is estimated to consume ~ 1-
20 2 % of the world's annual energy production of which 15 % of energy requirements are solely
21 consumed by high-pressure operations [5]. Currently, a considerable effort is centred upon the
22 development of highly active catalysts capable of accelerating ammonia synthesis reaction at
23 milder conditions and preferably at pressures aligned to those of green hydrogen produced by water
24 electrolysis (10 ~ 80 bar) [6]. From a thermodynamic point of view, producing ammonia at
25 pressures lower than those used in the H-B process is possible provided that the reaction is
26 conducted under low temperatures [7]. Thus, the development of novel generation of catalysts
27 capable of operating at milder conditions is an important milestone in the deployment of large-
28 scale Power to Ammonia process for energy storage.

1 Among the catalysts studied for ammonia synthesis, noble-metal based materials (e.g. Ru/graphite
2 and CoRe_4) have been reported to display superior catalytic activity when compared to the
3 industrial catalyst. [8] However, considering the cost of noble metals and their scarcity, there is
4 much interest in the development of non-noble metal-based catalyst for ammonia generation. One
5 of the most active catalysts reported in the literature is $\text{Co}_3\text{Mo}_3\text{N}$ ternary nitride (ammonia synthesis
6 rate of 330 - 652 $\mu\text{mol h}^{-1} \text{g}^{-1}$ at 400 °C and atmospheric pressure) [9] with catalytic performance
7 at high pressure exceeding the industrial H-B doubly promoted iron-based catalyst [10]. Hence,
8 there is a legitimate interest in further increasing the catalytic activity of $\text{Co}_3\text{Mo}_3\text{N}$. In the earlier
9 studies, the high catalytic activity of $\text{Co}_3\text{Mo}_3\text{N}$ was attributed to the presence of both Co and Mo
10 in the termination plan (*111*) resulting in an optimal N-binding energy [11]. Initially, the role of
11 nitrogen was believed to be limited to creating the right termination plan containing both Co and
12 Mo. However, recent studies shed the light on the mobility and reactivity of nitrogen in $\text{Co}_3\text{Mo}_3\text{N}$
13 via $^{15}\text{N}/^{14}\text{N}$ isotopic exchange studies and by DFT calculation pinpointing the potential role of the
14 lattice nitrogen in ammonia synthesis via routes akin to the Mars-van Krevelen (MvK) mechanism
15 [12-14]. Recently, the mobility and reactivity of lattice nitrogen, in binary and ternary nitrides,
16 towards hydrogen has been the focus of several research activities [15-17]. The capacity of some
17 metal nitrides (e.g. Ta_3N_5 , $\theta\text{-Mn}_6\text{N}_{5+x}$, AlN , Li_3N) to act as a source of pre-activated nitrogen has
18 been of high interest especially for the development of ammonia production by chemical looping.
19 In this approach, the lattice nitrogen reacts first with hydrogen to produce ammonia. The depleted
20 nitrogen transfer material is regenerated upon reaction with atmospheric N_2 in a second step.
21 Related to this concept, the nitrogen mobility and reactivity of several nitrogen transfer materials
22 have been explored including $\text{Mn}_6\text{N}_{5+x}$, AlN and Li_3N [18-20]. In several cases, the activity of
23 catalysts operating through mechanism akin to MvK was found to be strongly dependent upon: (i)
24 structural and textural properties (e.g. exposed surface and crystal size) (ii) chemical composition
25 and/or (iii) a combination of both [21, 22]. Unfortunately, the preparation of $\text{Co}_3\text{Mo}_3\text{N}$ requires at
26 least one calcination step at 550 °C to form the oxide precursor (CoMoO_4), once the oxide is
27 obtained, the nitride phase is formed by an ammonolysis step, under a flow of pure ammonia, at
28 750 °C. The different thermal treatments result in crystal growth and unavoidable surface reduction
29 ($\sim 10 \text{ m}^2 \text{ g}^{-1}$). As such, there is a high interest in the development of novel approaches for the
30 preparation of divided nitride phases, displaying high surface area and retaining small nanoparticle

1 size. At the nanoscale level, the catalytic activity is expected to increase due to the increase of the
2 surface to volume (A/V) atom ratio, which increases both available surface area and active site
3 density for catalytic reaction. Furthermore, ammonia synthesis reaction has been evidenced to be
4 structure-sensitive [23, 24]. Tsuji et al. demonstrated that the formation of bimetallic Co-Mo
5 nanoparticle supported on CeO₂, prepared by NaNaph driven reduction, resulted in higher catalytic
6 activity in ammonia synthesis [25]. The authors concluded that the formation of nitrogen vacancies
7 occurs more easily on Co-Mo nanoparticles when supported over ceria than for bulk Co₃Mo₃N.
8 Such vacancies formation can explain the better performances reported for Co-Mo/CeO₂ catalyst.
9 Thus, enhancing the surface concentration on steps and defects through the dispersion of active
10 nanoparticles nitrides is a tantalizing approach for improving the catalytic activity of nitrides
11 materials.

12 In this work, we implemented a novel strategy to improve the catalytic activity of Co₃Mo₃N by
13 confining the active phase within the mesopore of SBA-15 silica. SBA-15 was utilized as a suitable
14 support due to its: (i) high surface area; (ii) highly ordered and uniform mesopores; and (iii) good
15 thermal stability. The catalysts were evaluated in the ammonia synthesis reaction conducted at
16 400 °C and under atmospheric pressure. The effect of the textural and structural properties on the
17 physicochemical properties and catalytic activity was investigated through an extensive
18 characterization study. The positive effect of confining the active phase within the porosity of
19 SBA-15 was demonstrated in ammonia synthesis.

20 **2. Experimental**

21 **2.1. Catalyst Preparation**

22 **Chemicals.** All chemicals needed for the preparation of mesoporous SBA-15 support and
23 CoMo-N/SBA-15 materials were used as purchased without further purification:
24 tetraethylorthosilicate (Si(OC₂H₅)₄, TEOS, 98 wt.%, Sigma-Aldrich), non-ionic triblock
25 co-polymer Pluronic P123 (poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-
26 poly(ethylene glycol), average MW ~5800, Sigma-Aldrich), cobalt nitrate hexahydrate
27 (Co(NO₃)₂·6H₂O, 98 wt.%, Sigma Aldrich) and ammonium para-heptamolybdate tetrahydrate
28 (NH₄)₆Mo₇O₂₄·4.H₂O, 99 wt.%, Alfa Aesar).

1 **Preparation of Co₃Mo₃N.** Firstly, CoMoO₄ was prepared by dissolving the required quantities of
2 cobalt nitrate and ammonium heptamolybdate in deionized water. The solution was then heated
3 under reflux at 85 °C for 12 h. The resulting purple precipitate was recovered by filtration and
4 washed with deionized water and ethanol, followed by drying at 100 °C overnight. The powder
5 was then calcined at 500 °C (1.5 °C min⁻¹) for 6 h to form the desired CoMoO₄ phase. After
6 calcination, the oxide was converted to its nitride counterpart (Co₃Mo₃N) by an ammonolysis step.

7 **Preparation of CoMo-N/SBA-15 catalysts.** The SBA-15 support was prepared according to
8 hydrothermal method, under acidic conditions as described elsewhere [26].

9 CoMo/SBA-15 catalysts with different loadings were prepared by an adapted impregnation-
10 infiltration protocol. In the first step, Mo was impregnated on SBA-15 by incipient wetness
11 impregnation under mild drying (IWI) [27]. The aqueous molybdenum precursor solution was
12 mixed with the support and gently dried at 25 °C for 5 days. The solid was then calcined at 400 °C
13 (1.5 °C min⁻¹) for 5 h. At this step, SBA-15 supported MoO₃ is obtained. In a second step, cobalt
14 was added to the latter by Melt Infiltration (MI) method. In this method, the cobalt nitrate precursor
15 was first ground with Mo-SBA-15 powder. The resulting solid was then transferred into a
16 Teflon-lined autoclave and submitted to a thermal treatment at 57 °C for 4 days. The solid was then
17 calcined at 500 °C (5 °C min⁻¹) for 5 h.

18 **Ammonolysis process.** To convert the oxides into their nitrides counterpart, all the synthesized
19 materials were subject to an ammonolysis step under NH₃ (BOC, 99.98 wt.%) at a flow rate of
20 60 mL min⁻¹ at 785 °C for 5 h. Then, the material was cooled down to ambient temperature under
21 ammonia flow. Upon reaching room temperature, the catalyst was purged using N₂ (100 mL min⁻¹)
22 for 1 h followed by a passivation step under a low concentration of oxygen gas mixture (99.9 %
23 N₂/ 0.1 % O₂) for 5 h.

24 **N.B.** Herein, the samples obtained after the calcination step are denoted as X-CoMo/SBA-15. The
25 X represents the weight percentage of CoMoO₄. The catalysts obtained after the ammonolysis step
26 are denoted as X-CoMo-N/SBA-15, while post-reaction materials are referred to as
27 X-CoMo-N-Pr/SBA-15. The properties of SBA-15 were also studied and will be referred to as
28 N/SBA-15 for SBA-15 after ammonolysis, and N-Pr/SBA-15 for post-reaction material.

29

1 **2.2. Physical and textural characterizations**

2 **Powder X-ray diffraction (PXRD).** Wide angle PXRD patterns were collected using a Bruker X-
3 ray AXS D8 Advance diffractometer in Bragg-Brentano geometry configuration fitted with a
4 LynxEye Super Speed detector. XRD patterns were recorded with Cu K α radiation ($\lambda = 1.54184$
5 \AA) at 40 kV and 30 mA. Patterns are recorded over a 2θ range of 10-80 $^\circ$, at a step size of 0.02
6 $^\circ$ /step and a counting time of 0.5 s/step. Crystal phase identification was made by comparison with
7 the ICDD database.

8 **Small Angle X-ray Scattering (SAXS)** was performed on a Xeuss 2.0 (Xenocs) instrument
9 operating under vacuum with a GeniX3D microsource ($\lambda = 1.54184 \text{\AA}$) at 0.6 mA and 50 kV and
10 a 2D Pilatus 3R 200K detector.

11 **Nitrogen physisorption.** Textural properties were investigated from the adsorption/desorption
12 isotherms of N $_2$ recorded at -196 $^\circ\text{C}$ on a Micromeritics Tristar II automated gas sorption system,
13 operated with a software MicroActive version 4.06. Prior to the analysis, the catalysts were
14 outgassed under dynamic vacuum at 300 $^\circ\text{C}$ for 3 h. The specific surface area, S_{BET} , was calculated
15 from the linear part of the Brunauer-Emmett-Teller plot (10 points BET Method). The total pore
16 volume (V_{pore}) was determined on the plateau of the adsorption branch at $P/P_0 = 0.97$. The pore
17 size D_{BJH} , was evaluated using the Barret-Joyner-Halenda method applied to the adsorption branch
18 while the micropore volume (V_{micro}) was determined by the t -plot method.

19 **Solid State Nuclear Magnetic Resonance:** Samples obtained in powder form were separately
20 packed into either 7 mm or 1.3 mm (outer diameter) rotors. All 1D ^1H and 2D ^1H - ^1H correlation
21 experiments were performed on a Bruker Advance NEO4 800 MHz solid-state NMR spectrometer,
22 equipped with a 1.3 mm double-resonance magic-angle spinning (MAS) probe head with 50 kHz
23 magic-angle spinning (MAS), operating at room temperature. 1D ^1H MAS NMR spectra of all
24 samples were acquired with 32 co-added transients. 2D ^1H - ^1H spin diffusion spectra were acquired
25 with 80 t_1 FIDs, each with 4 co-added transients [28]. All ^1H chemical shifts are calibrated with
26 respect to neat TMS using adamantane as an external reference (^1H resonance, 1.85 ppm). All 1D
27 ^{29}Si MAS NMR experiments were performed on a Bruker Avance II 400 MHz equipped with a 7
28 mm double-resonance MAS probe head.

1 **X-ray photoelectron spectroscopy (XPS).** XPS spectra were recorded on a Kratos Analytical
2 AXIS Ultra DLD spectrometer employing a monochromatic Al K α X-ray radiation (1486.6 eV),
3 with an electron analyser operating in a fixed pass energy of 20 eV. All Binding Energies (BE)
4 were referenced to the carbon signal corresponding to C-C bonding in the C 1s core level at 284.8
5 eV. A pre-treatment chamber was used in order to mimic the catalytic pre-treatment, prior to
6 analysis, at 700 °C for 2 h under a 60 mL min⁻¹ flow of 75 vol.% H₂/N₂.

7 **Electron Microscopy (TEM).** Morphology analysis was performed using a TITAN Themis 300
8 S/TEM equipped with a high brightness Schottkey field emission gun, a monochromator and a
9 probe aberration corrector allowing energy and spatial resolution of about 150 meV and 70 pm,
10 respectively. The microscope is equipped with several annular dark field detectors and a super-X
11 detector system with four windowless silicon drift detectors for electron dispersive x-ray
12 spectroscopy (EDS). The experiments have been performed at 300 kV with semi-convergence
13 angle of about 20 mrad, probe size of the order of 500 pm and probe current between 60 and 100
14 pA. For high angle annular dark field (HAADF) imaging the collection angles have been between
15 50 and 200 mrad. EDS mapping has been obtained in spectrum imaging mode with dwell time per
16 pixel of about 15 μ m and continuously scanning frames until total acquisition time of about 15 to
17 20 minutes. All the samples were frozen at -120 °C in distilled water and then cut at 70 nm with an
18 ultramicrotome equipped with a 35° diamond knife (Leica UCT Ultracut). Cuts were then
19 deposited on a 200 mesh lacey carbon grid for analysis.

20 **Redox properties.** The reducibility of CoMo/SBA-15 was evaluated by means of Temperature
21 Programmed Reduction (H₂-TPR) experiment. The experiment was conducted on an Autochem
22 chemisorption analyser (Micromeritics). Prior to the reduction, the sample (50 mg) was pre-treated
23 under air flow (50 mL min⁻¹) at 200 °C for 1 h (10 °C min⁻¹) and then cooled to 25 °C. Thereafter,
24 temperature-programmed reduction was performed under a flow composed of 5 vol.% H₂ in Ar at
25 a total flow rate of 50 mL min⁻¹. The reduction was conducted from 25 °C to 1000 °C, with a
26 temperature ramp of 5 °C min⁻¹ and held for 30 min. Hydrogen consumption was recorded using a
27 TCD detector.

28 **Elemental analysis.** Nitrogen analysis was undertaken using a thermo scientific FlashSmart
29 automated elemental analyzer. The samples (~10 mg) were weighed in tin (Sn) containers and

1 introduced into the combustion reactor maintained at 950 °C and promoting dynamic flash
2 combustion of the sample. The resulting gases were quantified by a TCD detector.

3 **Catalytic activity:** In a typical temperature programmed reaction test, 0.150 g of CoMo-N/SBA-15
4 catalyst was placed in a quartz reactor and pre-treated at 700 °C under a 75 vol.% H₂/N₂ (BOC,
5 99.98 %) gas mixture at a total gas flow of 60 mL min⁻¹ for 2 h. The reaction was then performed
6 at 400 °C, under the same flow rate of 75 vol.% H₂/N₂ for at least 10 h. Ammonia production was
7 determined by measurement of the decrease in conductivity of a 200 mL 0.0018 M H₂SO₄ solution
8 through which the reactor effluent stream flowed and was monitored as a function of reaction time.
9 The rate of the reaction was calculated according to the following:

$$10 \quad r = \frac{\Delta_C \times n_{NH_3} \times 60}{m \times 10^{-6} \times X_{wt}}$$

11 Where: r is the rate of the reaction for a range of time; Δ_C is the average change in conductivity per
12 minute over a range of time; n_{NH₃} is the number of moles of ammonia that correspond to the
13 decrease of 1 μS/cm; m is the mass of the catalyst; X_{wt} is the load wt.%. The constants are added
14 for conversion purposes to obtain the rate in μmol/h. *g_{active phase}*

15 **Ammonia production under reducing condition.** Lattice nitrogen reactivity of the 10-CoMo-
16 N/SBA-15 towards hydrogen was evaluated under reducing condition. 0.6 g of catalyst was placed
17 in a quartz reactor and pre-treated at 700 °C under a 75 vol.% H₂/N₂ (BOC, 99.98 %) gas mixture
18 at a total gas flow of 60 mL min⁻¹ for 2 h. Therefore, the reactor was purged under argon and the
19 temperature decreased at 400°C. The reaction was then performed at 400 °C, under the same flow
20 rate under a 5 vol.% H₂/Ar for at least 10 h. Low H₂ concentration flow was applied in order to
21 decrease the N consumption rate from the catalyst. Quantification of ammonia was done in a similar
22 manner to the catalytic test.

23

24 **3. Results and Discussion**

25 **3.1. Structural and textural properties of CoMo-N/ SBA-15**

26 **3.1.1. Stability of SBA-15 under reactive conditions**

1 **PXRD.** While the properties of SBA-15 support are extensively studied, the stability of this latter
2 under ammonolysis conditions and under conditions relevant to ammonia synthesis is less available
3 in the literature. In order to verify the stability of SBA-15 support through the different steps of the
4 synthesis, SAXS patterns of the as-prepared siliceous support were first collected before and after
5 nitridation and are presented in Fig. S1. As expected, the as-prepared siliceous support displays the
6 characteristic three well-resolved diffraction peaks that can be associated to the (100) , (110) , and
7 (200) planes of the $p6mm$ hexagonal symmetry structure reflecting the well-defined and uniform
8 range mesoporous structure of SBA-15 (Fig. S1-a). After ammonolysis treatment, the support
9 maintained its pore structure quality (Fig. S1-b) albeit a shift of the reflection peaks can be observed
10 at higher 2θ angles from 0.889° to 0.933° . This shift indicates a slight pore contraction of the
11 sample and could originate from the sintering occurring during the ammonolysis process (785°C).
12 Nevertheless, as illustrated in Fig. S1-c, SBA-15 support still presents its characteristic reflections
13 after 10 h of reaction under conditions relevant to ammonia synthesis (75 vol.% H_2 in N_2 at a total
14 flow rate of 60 mL min^{-1} , 400°C) indicating the conservation of a good pore structure ordering
15 within the sample.

16 **N_2 adsorption/desorption.** Complementary information on the impact of the ammonolysis
17 treatment on the textural properties of SBA-15 was obtained through nitrogen physisorption
18 analysis (Table 1 and Fig. S2). Before treatment, SBA-15 exhibited an adsorption/desorption
19 isotherm of type IV with a hysteresis loop of type H1, at a relative pressure between $P/P_0 = 0.6 -$
20 0.8 , which is typical of a mesoporous solid with highly uniform arrays of cylindrical pores with an
21 average diameter of 6.5 nm (Fig. S2-a). After ammonolysis, the study of the isotherm profile
22 confirmed that N/SBA-15 maintained a uniform mesoporosity (Fig. S2-b). However, an important
23 decrease of 33 % in the SBA-15 accessible surface area ($760\text{ m}^2\text{ g}^{-1}$ to $504\text{ m}^2\text{ g}^{-1}$), accompanied
24 by a decrease in pore volume ($1.12\text{ cm}^3\text{ g}^{-1}$ to $0.75\text{ cm}^3\text{ g}^{-1}$) are observed. Moreover, upon
25 ammonolysis, N/SBA-15 was found to contain smaller pores with size centred around 6.1 nm
26 which is in line with pore contraction observed by SAXS. These changes might be related to the
27 sintering at high temperature or to the corrosive and basic atmosphere of the ammonolysis process.
28 However, no significant changes in the textural properties of the support were detected under
29 ammonia synthesis reaction conditions (Fig. S2-c).

1 **TEM.** The morphology of the N/SBA-15 material was observed by means of HRTEM. The images
2 (Fig. S3) show the well-ordered hexagonal arrays of the mesopores, confirming that after
3 ammonolysis step, the characteristic porous structure of SBA-15 material is maintained as
4 previously indicated by SAXS and N₂ porosimetry results. Accumulation of nitrogen on the support
5 is evidenced, through elemental mapping. This accumulation is also confirmed by N chemical
6 analysis through elemental analysis (CHN), which gives a N content in the material of ~ 2.74 wt.%.
7

8 **Solid-state ²⁹Si and ¹H NMR spectroscopy.** Fig. 1 presents 1D ²⁹Si MAS NMR spectra of the as
9 prepared SBA-15 (post-calcination), N/SBA-15 (post-ammonolysis) and N-Pr/SBA-15 (post-
10 reaction). In the ²⁹Si NMR spectrum of SBA-15, peaks at -90, -100, and -110 ppm that can be
11 attributed to Si-(OSi)₂(OH)₂ units (Q²), Si-(OSi)₃(OH) units (Q³), and Si-(OSi)₄ units (Q⁴),
12 respectively are observed [29]. After ammonolysis, the overall line-shape of ²⁹Si NMR spectrum
13 associated with the Q², Q³ and Q⁴ sites was retained to some degree, but slightly shifted towards
14 high frequency values (Q²: -89, Q³: -100, and Q⁴: -109 ppm). However, the relative peaks
15 intensities are different. In addition, these peaks are broader which may be related to the
16 heterogeneity of the Si local field (non-uniform distribution of bond length and angles) after
17 ammonolysis. More importantly, an additional strong intensity resonance at ca. -71 ppm and a
18 weak intensity broad peak in the vicinity from -75 ppm to -60 ppm are expected to originate from
19 the formation of surface silanol by ammonia to surface silyl-amine site (SiO₂N(NH)_x) moieties
20 [29]. However, the extent of these surface sites is likely limited as reflected in the low intensity
21 peak. The complete formation of an amorphous silicon nitride Si₃N₄ can be safely ruled out from
22 these results as the spectra obtained for these materials are usually characterised by large peak with
23 maxima of ~ 48 ppm, which is not observed in the ²⁹Si MAS NMR spectra [30]. Elemental analysis
24 further corroborates NMR results and confirms the low nitrogen content in the sample ~ 2.74 wt.%.
25 In the post-reaction SBA-15 catalyst, minor changes in ²⁹Si NMR are observed as the intensity
26 ratio of Q²/Q³ is slightly different, with respect to the post-ammonolysis sample, which may be
27 related to differences in silanol concentration in both samples.

28 Furthermore, calcined, post-ammonolysis, and post-reaction SBA-15 were studied using ¹H-¹H 2D
29 spin diffusion (SD) NMR to characterise through-space ¹H-¹H proximities. In measurements of
30 this type, magnetization is allowed to exchange between the ¹H neighbouring sites using a mixing

1 delay (as referred to as spin diffusion delay), which leads to the on- and off-diagonal peaks for
2 chemically equivalent and inequivalent ^1H sites, respectively. Fig. 2 displays 1D ^1H MAS and 2D
3 ^1H - ^1H SD spectra of SBA-15 before and after the reaction. Prior to the ammonolysis treatment, the
4 ^1H NMR spectrum of calcined SBA-15 is mainly dominated by a major peak at ~ 3.8 ppm
5 corresponding to the surface adsorbed water, and a broad distribution of weak intensity peaks
6 centered at 6.5 ppm are attributable to the strong hydrogen bonding interactions between these
7 groups and silanol protons. In the 2D ^1H - ^1H SD spectrum of the same material (Fig. 2b), the off-
8 diagonal peak between 3.8 ppm and 6.5 ppm indicate the through space proximity between silanol
9 and the hydrogen bonded hydroxyl moieties. By comparison, after ammonolysis, and in the post-
10 reaction material, the ^1H peak associated with silanol groups is displaced towards high frequency
11 values (4.5 ppm and 5.2 ppm) with this latter peaks is hypothesized to originate from weakly
12 adsorbed silyl-amine sites [31-33]. In addition, a broad peak between 0 and 4 ppm appeared after
13 ammonolysis which is likely due to the formation of silanol groups (SiOH) at different local
14 chemical environments [32]. Further changes are observed after the post-reaction, whereby the
15 intensities of peaks in the 0-4 ppm range (SiOH groups) are increased with respect to the
16 water/silanol protons (4.2 ppm) which is consistent with the increased intensities of Q^3 and Q^2
17 silicon sites observed in ^{29}Si NMR spectra. The increase in silanol concentration is likely due to
18 the reaction between Si-O-SiO(OH) and NH_3 which leads to the formation of OSiOH and
19 $\text{H}_2\text{NSiO(OH)}$. Additionally, subtle changes to the lineshape at 5.2 and 5.7 ppm are observed with
20 partially resolved shoulder peaks are expected to stem from the NH_3 -like groups adsorbed on the
21 SBA-15 [33, 34]. This is further supported by the analysis of 2D SD spectra of ammonolysis and
22 post-synthesis reaction (Fig. 2c, d) in which strong correlation peaks between the surface adsorbed
23 water and the silyl-amine sites are observed, as depicted in the blue circles. The off-diagonal 2D
24 peaks connecting the chemical shifts at 1.3 and 1.8 ppm and 4.5 ppm (grey boxes) are due to the
25 close proximities between the surface adsorbed water and the silanol groups.

26 Overall, structural and textural properties of the SBA-15 support was indubitably impacted by the
27 reactive conditions applied in the study. However, it was observed that N/SBA-15 maintained its
28 ordered porous structure and satisfying surface area $\sim 504 \text{ m}^2 \text{ g}^{-1}$, which is still fairly high for
29 catalytic applications. Besides, changes in the local Si environment were evidenced by ^{29}Si and ^1H
30 NMR and could be attributed to the formation of silyl-amine sites ($\text{SiO}_2\text{N}(\text{NH})_x$) on the silica

1 surface. In the other hand, HRTEM and SAXS results clearly indicate that N/SBA-15 maintain the
2 initial characteristics of a 2D hexagonally ordered structure. Thus, we demonstrate that SBA-15 is
3 sufficiently robust under reaction conditions and is to be considered as an appropriate support for
4 the dispersion of small metal nitride particles within its porosity.

6 **3.1.2. Characterization and Structural Evolution of CoMo/SBA-15 and CoMo-N/SBA-15**

7 **PXRD. Bulk $\text{Co}_3\text{Mo}_3\text{N}$ catalyst.** Before ammonolysis, the presence of a pure and well crystallized
8 CoMoO_4 precursor phase (PDF: 21-0868) was confirmed by PXRD (Fig. S4). The diffractogram
9 exhibited intense and sharp PXRD diffraction peaks indicating the preparation of a well-
10 crystallized material with a large coherent diffraction domain. Following the ammonolysis step, all
11 the detected XRD diffraction peaks (Fig. 3) matched the $\text{Co}_3\text{Mo}_3\text{N}$ (PDF 89-7953) confirming the
12 formation of a pure nitride phase. As in the case of CoMoO_4 intense and sharp reflections XRD
13 peaks are observed indicating the formation of a well-crystallized nitride phase.

14 **CoMo/SBA-15 catalysts.** Prior to the ammonolysis step, the effective dispersion of CoMoO_4 phase
15 in SBA-15 was confirmed by PXRD in the wide-angle domain (Fig. S4) for which only poorly
16 defined reflections of the oxide phase are observed despite loading reaching 30 wt.% in the
17 supported catalysts. Interestingly, after the ammonolysis step, no peaks related to either $\text{Co}_3\text{Mo}_3\text{N}$
18 phase or single Co-N / Mo-N phases were detected on supported samples. Only a broad PXRD
19 peak of amorphous silica was retained (Fig. 3-a). The absence of reflections related to the $\text{Co}_3\text{Mo}_3\text{N}$
20 phase may be related to a possible re-dispersion of this latter during ammonolysis process. The
21 presence of single Co-N or Mo-N phases can however not be ruled out, even if the broad signal
22 positions below the main reflections of the $\text{Co}_3\text{Mo}_3\text{N}$ bulk phase. SAXS patterns collected after the
23 ammonolysis step displayed the same diffraction patterns, with respect to the parent N/SBA-15,
24 confirming that the derived catalysts maintained their regular pore structure through ammonolysis
25 conditions (Fig. 3-b).

27 **Nitrogen adsorption-desorption analysis**

28 The evolution of the textural properties of the catalysts was investigated by means of N_2
29 physisorption. The results are shown in Fig. 4, Fig. S5, and Table 1.

1 **Bulk CoMoO₄ and Co₃Mo₃N.** The unsupported CoMoO₄ and Co₃Mo₃N materials exhibited a
2 limited accessible specific surface area (Table 1). After the ammonolysis, the surface area increased
3 slightly from 6.1 m²g⁻¹ on CoMoO₄ to 13 m²g⁻¹ on the Co₃Mo₃N counterpart. Both materials
4 exhibited a type II isotherm reflecting their non-porous nature.

5 **CoMo/SBA-15.** The N₂ adsorption/desorption isotherms of CoMo/SBA-15 (10, 20 and 30 wt.%
6 of CoMo) are presented in Fig. S5. 10-CoMo/SBA-15 and 20-CoMo/SBA-15 preserve a similar
7 type IV isotherm with a hysteresis loop of type H1 with respect to the parent SBA-15. Furthermore,
8 only a small increase in the pore size from 6.5 nm on SBA-15 to ~ 7.2 nm on 20-CoMo/SBA-15
9 was observed. These results confirm that these catalysts retain the initial characteristics of SBA-15.
10 However, the 30-CoMo/SBA-15 showed an H2b hysteresis loop, reflecting pore blocking at high
11 CoMo loading. Compared to the SBA-15, the BET surface area of CoMo/SBA-15 catalysts showed
12 a marked decrease with CoMo loading (from 760 m² g⁻¹ on SBA-15 to 295 m² g⁻¹ on 30-CoMo-
13 SBA-15 sample, see Table 1), indicating the filling of CoMoO₄ in the channels of SBA-15.

14 **CoMo-N/SBA-15:** The N₂ adsorption/desorption isotherms obtained after the ammonolysis step
15 are presented in Fig. 4. The results confirm that, at low CoMo loading, the ordered mesoporous
16 structure is mostly not altered by the ammonolysis step, while the microporous domain is strongly
17 reduced (Table 1). Interestingly, in the CoMo-N/SBA-15, the changes, upon ammonolysis, are less
18 significant than those observed on the bare SBA-15. In fact, only a small decrease in the accessible
19 surface area and pore volume occurring over CoMo-N/SBA-15 is observed which might be due to
20 the presence of nanoparticles inside SBA-15 mesoporosity.

21

22 **TEM-EDS analysis**

23 After ammonolysis, the morphology of CoMo-N/SBA-15 as well as the local distribution of cobalt
24 and molybdenum species in mesoporous SBA-15 were studied by means of HAADF-STEM
25 analysis coupled with EDS mapping. A selection of representative images of the supported samples
26 is presented in Fig. 5 and Fig. S6.

27 As observed on the slice analyses (~75 nm thickness), the characteristic porous structure of SBA-15
28 material is preserved with well-ordered mesoporous hexagonal arrays in all CoMo-N/SBA-15
29 which is consistent with SAXRD and N₂ physisorption. Furthermore, the distribution profile of the

1 metal species throughout the porosity of SBA-15 was observed by HAADF micrographs performed
2 over various areas of the supported samples. As observed, nanoparticles are highly dispersed within
3 the 2D-channels of SBA-15 for the 10-CoMo-N/SBA-15 catalyst (Fig 5 and Fig. 6-a).
4 Complementary EDS analysis confirm the high dispersion of Co and Mo species throughout the
5 siliceous framework albeit some enrichment of metal species on the external surface of the grain
6 cannot be ruled out (Fig. S6). The progressive increase of CoMo amount within the SBA-15
7 support could slightly amplify such external Co enrichment that is more noticeable especially on
8 30CoMo-N/SBA-15 (Fig. S6-c), due to the first Mo incorporation in the support that can lead to
9 some pore entrance constriction thus limiting the infiltration of Co precursors. Therefore, Co_3O_4
10 phase was identified by PXRD (Fig. S4) as a segregated secondary phase on the oxide material
11 (30-CoMo/SBA-15). However, most of the Co and Mo signatures in the EDS micrographs are in
12 close proximity, supporting the formation of CoMo-N mixed phase instead of single Co-N and Mo-
13 N phases.

14

15 **Oxidation states and chemical composition by XPS.**

16 To gain insight into the evolution of the surface chemical composition, XPS analysis was
17 performed for the calcined and post-ammonolysis catalysts. Furthermore, the effect of catalytic
18 pre-treatment on the oxidation state and surface composition was also studied. The results are
19 summarized in Fig. 6, Table S1, Table S2, and Fig. S7.

20 **$\text{Co}_3\text{Mo}_3\text{N}$.** As expected, in CoMoO_4 , the predominant species are Co^{2+} and Mo^{6+} (Table S1 and
21 Table S2). However, after the ammonolysis step, Mo 3d and Co 2p XPS profiles showed a range
22 of different oxidation states similar to those reported in the literature with the presence of Mo-O
23 and Co-O [35]. The spectral decomposition of the high-resolution Mo 3d region can be ascribed to
24 the Mo^{6+} , Mo^{5+} , Mo^{4+} and Mo-N species. The peaks characteristics of Mo-N species are of weaker
25 intensity suggesting the formation of an oxidation layer at the surface of $\text{Co}_3\text{Mo}_3\text{N}$. These results
26 are consistent with the oxidation layer observed by HAADF-STEM (Fig. S8) which was passivated
27 after the ammonolysis step.

28 In order to access the surface composition of the catalyst under reaction conditions, $\text{Co}_3\text{Mo}_3\text{N}$ was
29 pre-treated in an XPS environmental chamber permitting to mimic the pre-treatment used prior the
30 catalytic test. The use of an environmental chamber allowed us to study the surface composition of

1 $\text{Co}_3\text{Mo}_3\text{N}$ with minimal surface contamination. A drastic change was observed in both Mo 3d and
2 Co 2p XPS profiles. After the pre-treatment under a flow of H_2/N_2 , an important shift to lower
3 binding energies is observed in both Co and Mo XPS profiles. These values are more aligned with
4 the intermetallic nature of $\text{Co}_3\text{Mo}_3\text{N}$ presenting a low valent state of metals. The high resolution of
5 Mo 3d spectra (Fig. 6) show two major spectral lines corresponding to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ spin-
6 orbit components 228.59 eV and 231.73 eV of Mo-N species [25, 35]. The intensity and fraction
7 of Mo-N is much pronounced in this case revealing the true composition of the active surface phase
8 under reaction conditions. In the high-resolution Co 2p spectra, the position of the major spectral
9 line was found at 778.88 eV which is in agreement with the value reported in $\text{Co}_3\text{Mo}_3\text{N}$ prepared
10 by Hosono's group [25]. Although this value is very close to metallic cobalt, this latter is usually
11 reported at lower binding energy (777.9 eV).

12 Fig. 6 shows the spectral decomposition of high-resolution Mo 3p spectra in which N 1s can also
13 be observed. In this region, an intense and well resolved peak is observed at 398.4 eV which is
14 very comparable to N 1s observed in $\text{Co}_3\text{Mo}_3\text{N}$ (397,9 eV) and in Mo_2N and MoN bulk (397.8 eV)
15 [25, 36]. Thus, after the pre-treatment, it can be concluded that the surface is mostly populated with
16 N adatoms.

17 **CoMo-N/SBA-15:** The evolution of the surface composition of CoMo-N/SBA-15 catalysts were
18 studied and compared to the unsupported catalyst (Fig. 6, Fig. S7, Table S1, and Table S2). In a
19 similar manner to CoMoO_4 , all the CoMo/SBA-15 obtained after calcination were composed
20 predominantly of Mo^{6+} and Co^{2+} species. For 30-CoMo/SBA-15, an additional set of peaks were
21 identified in the Co 2p spectra at 779.4, 780.70, 782.00, 785.00 and 789.30 eV, corresponding to
22 Co_3O_4 [37] (Fig. S7) which is in line with PXRD results. Such signals were not observed for 10-
23 CoMo/SBA-15 sample, confirming the absence of Co_3O_4 formation in this solid in agreement with
24 PXRD results.

25 Upon ammonolysis, all the catalysts showed a range of oxidation states that are similar to those
26 observed in the unsupported $\text{Co}_3\text{Mo}_3\text{N}$. For instance, the spectral decomposition of the high-
27 resolution Mo 3d region showed the presence of a range of oxidation state including Mo^{6+} , Mo^{5+} ,
28 Mo^{4+} and Mo-N. For the 30-CoMo-N/SBA-15, Co_3O_4 peaks are not observed after ammonolysis,
29 suggesting that the latter has been successfully nitrated (Table S2). After the pre-treatment, most
30 of the materials were composed of Mo-N and Co-N confirming that under reaction conditions, the

1 surface is mainly populated with N adatoms. In summary, the surface composition of CoMo-
2 N/SBA-15 was found to be very similar to the $\text{Co}_3\text{Mo}_3\text{N}$.

3

4 **Reducibility of CoMo/SBA-15**

5 The degree of interaction between the dispersed phase and SBA-15 support can be indirectly
6 evaluated upon studying the reduction of cobalt molybdenum oxide species by H_2 -TPR. The
7 H_2 -TPR results of CoMo/SBA-15 catalysts are presented in Fig. 7 and in Table S3. alongside the
8 CoMoO_4 .

9 The reduction temperature and H_2 consumption are presented in Table S3. TPR-profile of CoMoO_4
10 showed that the reduction process started at 600 °C. The reduction profile was characterized by
11 two main reduction peaks at 628 and 872 °C with a smaller shoulder at 710 °C. The H_2 -TPR profile
12 agrees well with previous studies where the reduction of CoMoO_4 is generally accompanied with
13 the formation of suboxides intermediates such as $\text{Co}_2\text{Mo}_3\text{O}_8$ and/or CoMoO_3 [38, 39]. Substantial
14 changes in the reduction behaviour are observed for the CoMo/SBA-15 samples. The reduction
15 peaks are shifted to lower temperatures, with reduction starting at temperatures as low as 450 °C.
16 In this case, the reduction peak at lower temperature which presents higher intensity and the
17 shoulder between both main peaks is no longer observed. Interestingly, the main reduction peak
18 slightly shifted to higher temperatures with the increase in CoMo loading. For the 30-
19 CoMo/SBA15 sample, an additional peak is observed at a temperature of ~ 338 °C which might be
20 attributed to the reduction of segregated Co_3O_4 phase, previously identified by PXRD analysis [40].
21 In summary, the reactivity of cobalt molybdates towards hydrogen was greatly improved upon
22 dispersion on SBA-15, confirming the stabilisation of small nanoparticles within the siliceous
23 framework.

24 **3.2. Catalytic performance in ammonia synthesis**

25 The catalytic activity of N/SBA-15 was first evaluated (Fig. 8 and Fig. 9). After 10 h of reaction,
26 no ammonia production was measured which ruled-out the possibility of ammonia
27 formation/desorption from the silylamine sites observed by ^{19}Si and ^1H NMR. Thereafter, the
28 catalytic activity of CoMo-N/SBA-15 was studied and compared to the well-established $\text{Co}_3\text{Mo}_3\text{N}$
29 catalyst. $\text{Co}_3\text{Mo}_3\text{N}$ exhibits high catalytic activity for ammonia synthesis at ambient pressure (rate

1 of $248 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$, WHSV $24\,000 \text{ mL g}^{-1} \text{h}^{-1}$) which is consistent with values reported in the
2 literature but at lower WHSV $9\,000 \text{ mL g}^{-1} \text{h}^{-1}$ [41, 42]. However, it is worth noting that increasing
3 WHSV might affect ammonia synthesis rate, and therefore a direct comparison of activity with
4 values from the literature is difficult. Under the same catalytic testing conditions, the 10-CoMo-
5 N/SBA-15 (rate of $263 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$, WHSV $24\,000 \text{ mL g}^{-1} \text{h}^{-1}$) exhibits close initial catalytic
6 activity than for the $\text{Co}_3\text{Mo}_3\text{N}$, despite a significantly lower content of active phase in the reactor.
7 When the active phase loading increases up to 20 wt.%, almost a linear increase in the catalytic
8 activity was observed (20-CoMo-N/SBA-15: $479 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$, WHSV $24\,000 \text{ mL g}^{-1} \text{h}^{-1}$).
9 Increasing the loading of the active phase to 30 wt.%, resulted in a further increase in the catalytic
10 activity up to $518 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$. However, upon reaction, differences between initial catalytic
11 activity and activity after reaching steady state conditions are observed (Table 2). The supported
12 CoMo-N/SBA-15 displayed a stationary rate of 120, 200 and $170 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ corresponding
13 to the loadings of 10, 20, 30 wt.% respectively. It can be seen that the stationary ammonia synthesis
14 rate is lower than the initial rate which may denote the contribution of surface nitride
15 decomposition by hydrogenation during the first hour of reaction. The decrease in the catalytic
16 activity is more apparent with the 30-CoMo-N/SBA-15 which might be related to the presence of
17 a single phase of cobalt prone to decomposition and deactivation.

18 The beneficial effect of the CoMo-N phase dispersion becomes more evident when ammonia
19 synthesis rate is normalised with respect to the active phase loading (wt.% of $\text{Co}_3\text{Mo}_3\text{N}$ phase). For
20 instance, at steady state conditions, a rate of $1714 \mu\text{mol g}_{\text{active phase}}^{-1} \text{h}^{-1}$ is obtained over the 10-
21 CoMo-N/SBA-15 catalyst. A gradual decrease is observed while increasing the cobalt
22 molybdenum charge. Thus, the normalized ammonia synthesis rate decreased to $1429 \mu\text{mol g}_{\text{active}}$
23 $\text{phase}^{-1} \text{h}^{-1}$ and $810 \mu\text{mol g}_{\text{active phase}}^{-1} \text{h}^{-1}$ for the 20-CoMo-N/SBA-15 and 30-CoMo-N/SBA-15
24 catalysts respectively. All values however remain far above the production rate registered for bulk
25 $\text{Co}_3\text{Mo}_3\text{N}$ ($248 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$). From these results, it can be concluded that the stabilization of
26 cobalt molybdenum nitride at a nanoscale level ameliorates significantly its catalytic performance
27 in ammonia synthesis. The progressive decrease in normalized ammonia synthesis rate with the
28 CoMo-N loading could be linked to the pore plugging phenomenon that becomes more significant
29 at high loading. Indeed, we observe a decrease of the normalised ammonia synthesis rate by 53%
30 between 10% and 30% CoMo-loading. At the same time, the surface area and pore volume of the

1 catalysts are reduced by 43% and 51% respectively. Consequently, the decrease of active phase
2 reactivity is preferably associated to the decrease in particle accessibility inside the pores than to a
3 reduction of the nitride phase surface/bulk reactivity.

4 **Thermal, textural, and structural stability of CoMo-N/SBA-15 catalysts after reaction.**

5 The thermal stability of CoMo-N/SBA-15 catalysts is a significant challenge, especially under
6 ammonia synthesis condition. To provide a distinct comparison between post-ammonolysis and
7 post-reaction catalysts, a systematic study on the thermal stability of catalysts has been conducted.
8 Fig. 10-a shows the PXRD patterns recorded in the wide-angle domain, for the post-reaction
9 CoMo-N/SBA-15 samples. After 10 h of reaction, no well-defined peaks related crystalline
10 $\text{Co}_3\text{Mo}_3\text{N}$ are detected denoting the stability of the $\text{Co}_3\text{Mo}_3\text{N}$ phase formed under ammonia
11 synthesis conditions. Indeed, the small broad peak observed at $2\theta \sim 43^\circ$ might be related to the
12 presence of nitride phase, crystallizing at the nanoscale level or that remain not crystallized. SAXS
13 patterns collected at low angle domain shows the typical diffraction peaks related to the (100),
14 (110), and (200) planes of the p6mm hexagonal SBA-15 symmetry structure showing that the
15 support maintained its uniform pore structure under ammonia synthesis conditions (Fig. 10-b).

16 The N_2 adsorption/desorption isotherms of CoMo-N-Pr/SBA-15 samples are presented in Fig. 11.
17 After the catalytic reaction, the 10-CoMo-N-Pr/SBA-15 and 20-CoMo-N-Pr/SBA-15 catalysts
18 maintained their isotherms of type IV with a hysteresis loop of type H1, characteristic of highly
19 ordered structures with uniform disposition of cylindrical pore. Furthermore, only minor changes
20 in the surface area and pore volume are observed between the post-ammonolysis and post-reaction
21 catalyst, thus showing the good textural and structural stability of CoMo-based nitrides when
22 supported on SBA-15. However, the 30-CoMo-N-Pr/SBA-15 showed a more pronounced surface
23 reduction (285 to 213 m^2g^{-1}) which might be related to structural collapse or eventually minor
24 sintering of nitride particles occurring on external surface of silica grains.

25 **3.3. Discussion**

26 In the literature, the high catalytic activity of $\text{Co}_3\text{Mo}_3\text{N}$ in ammonia synthesis has been correlated
27 to the presence of active crystallographic faces that contains both Co and Mo components resulting
28 in optimal binding energy with N_2 . Initially, the role of nitrogen was believed to be limited to the
29 creation of the appropriate surface termination planes (111). However, experimental work,

1 enhanced by DFT-calculation, highlighted that $\text{Co}_3\text{Mo}_3\text{N}$ might operate via the Mars-van Krevelen
2 mechanism in which the lattice nitrogen in metal nitrides being the active species in ammonia
3 synthesis. In this mechanism, lattice nitrogen is directly hydrogenated yielding ammonia and
4 nitrogen lattice vacancy [43]. The nitrogen vacancy can afterwards activate molecular nitrogen to
5 regenerates the active site. Furthermore, Zeinalipour-Yazdi *et al.* demonstrated via DFT
6 computational study that $\text{Co}_3\text{Mo}_3\text{N}$ contains a high concentration of nitrogen vacancies (1.6×10^{16}
7 to $3.7 \times 10^{16} \text{ cm}^{-2}$) that can adsorb and activate N_2 in conditions relevant to ammonia synthesis.
8 Furthermore, Tsuji *et al.* reported enhanced catalytic activity of Co-Mo nanoparticles when
9 supported on CeO_2 . The better performance of Co-Mo/ CeO_2 catalyst was explained on the basis of
10 nitrogen vacancies more easily stabilized in the Co-Mo nanoparticles than in bulky $\text{Co}_3\text{Mo}_3\text{N}$
11 crystals [25]. In this context, the generation of cobalt molybdenum nanoparticles is of high interest
12 due to its high surface area to volume ratio and the high proportion of accessible surface atoms. In
13 the current investigation, the XPS study indicates a close surface composition of the
14 CoMo-N/SBA-15 to $\text{Co}_3\text{Mo}_3\text{N}$. However, strong disparities exist between $\text{Co}_3\text{Mo}_3\text{N}$ and
15 CoMo-N/SBA-15 in terms of structural and textural properties. For instance, all the catalysts
16 showed high surface area with respect to the unsupported $\text{Co}_3\text{Mo}_3\text{N}$ catalyst (up to 10 times higher).
17 Furthermore, no XRD diffraction peaks were observed at high angle domain confirming the high
18 dispersion of the active phase in SBA-15 structure. These findings are supported with TEM which
19 reveals the formation of cobalt molybdenum nanoparticles stabilized within the mesopores of
20 SBA-15. As demonstrated from the catalytic activity measurement, CoMo-N/SBA-15 displays an
21 intrinsically high catalytic activity towards ammonia production (10-CoMo-N/SBA-15: $1714 \mu\text{mol}$
22 $\text{g}_{\text{active phase}}^{-1} \text{h}^{-1}$, 20-CoMo-N/SBA-15: $\mu\text{mol g}_{\text{active phase}}^{-1} \text{h}^{-1}$, and 30-CoMo-N/SBA-15: $810 \mu\text{mol g}$
23 $\text{active phase}^{-1} \text{h}^{-1}$) when compared to the unsupported catalyst ($298 \mu\text{mol g}^{-1} \text{h}^{-1}$). The increase in reaction
24 rates is seemingly consistent with the increase in accessible surface area and crystal size reduction
25 observed by S/TEM. A parallel can be established with oxides (e.g. perovskite, hexaaluminate)
26 operating via MvK mechanism, where previous studies, demonstrated an important increase in
27 oxygen mobility with the decrease in crystal size leading to enhanced catalytic activities [44].
28 Furthermore, the mobility of lattice nitrogen and its reactivity in 10-CoMo-N/SBA-15 was
29 confirmed under reducing conditions using 60 mL min^{-1} flow of 5 vol.% H_2 : Ar. Upon reaction,
30 ammonia production in the absence of dinitrogen, was confirmed at 400°C (Fig. S9). Thus, the

1 amount of ammonia produced can be directly linked to lattice nitrogen reacting with hydrogen. The
2 process however, occurs in two steps, the first step suggesting the reduction of $\text{Co}_3\text{Mo}_3\text{N}$
3 nanoparticle into $\text{Co}_6\text{Mo}_6\text{N}$ as seen in the literature [45], followed by a second step transforming
4 the reduced nitride into intermetallic phase. This mechanism is supported PXRD and HRTEM
5 images coupled with EDS and FFT performed over post-reaction 10-CoMo-N/SBA-15 sample with
6 evidence of formation of the intermetallic $\text{Mo}_{0.25}\text{Co}_{0.75}$ phase (PDF number: 04-018-9512) (Fig.
7 S10 and Table S4). The reduction process in the supported nitrides resulted in the formation of
8 $\text{Mo}_{0.25}\text{Co}_{0.75}$ intermetallic phase, whereas unsupported $\text{Co}_3\text{Mo}_3\text{N}$ was only reported to reduce to
9 the $\text{Co}_6\text{Mo}_6\text{N}$, which might suggest that the lattice nitrogen mobility and reactivity is crystallite
10 size dependent. This would be consistent with the improved catalytic activity of CoMo-N/SBA-15
11 catalysts operating via MvK mechanism. It is also noteworthy, that beyond the improvement of
12 nitrogen mobility in nanoparticles, given the structure-sensitivity of ammonia synthesis reaction,
13 the performance of CoMo-N/SBA-15 could also results from an increase the high proportion of
14 accessible surface atoms and/or increases in steps and nitrogen defects in the surface.

15 **Conclusion**

16 In summary, SBA-15 was found to be a robust support for ammonia synthesis reaction displaying
17 good thermal and chemical stability under ammonolysis and ammonia synthesis reaction
18 conditions. CoMo-N/SBA-15, with different loadings, was successfully prepared by two
19 consecutive impregnation steps. The results of characterization demonstrate a high dispersion of
20 metal nitrides within SBA-15 resulting in improved textural and structural properties. Although,
21 changes in the local Si environment due to the formation of silyl-amine sites were evidenced by
22 ^{29}Si and ^1H NMR upon ammonolysis, SBA-15 was found to be stable enough to maintain an
23 ordered porous structure and high surface area $\sim 504 \text{ m}^2 \text{ g}^{-1}$ for catalytic application. XPS analysis
24 revealed that the surface composition of CoMo-N/SBA-15 catalysts is similar to the non-supported
25 $\text{Co}_3\text{Mo}_3\text{N}$ which is a paramount condition to develop high catalytic activity for ammonia synthesis.
26 Because of their structural properties, i.e. a reduced crystal size and a high level of dispersion for
27 the nitride phase, all CoMo-N/SBA-15 (10, 20 and 30 wt.%) displayed enhanced catalytic activity
28 in ammonia synthesis (1714 , 1429 and $810 \mu\text{mol g}_{\text{active phase}}^{-1} \text{ h}^{-1}$ respectively) with respect to the
29 $\text{Co}_3\text{Mo}_3\text{N}$ catalyst ($298 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$). The lattice nitrogen mobility and reactivity towards

1 hydrogen in the supported CoMo-N/SBA-15 was also demonstrated under reducing condition, in
2 the absence of dinitrogen, which indicative of ammonia synthesis occurring via mechanism similar
3 to MvK. The enhanced catalytic activity originates probably from improving nitrogen mobility
4 and/or alteration of the surface composition (*e.g.* vacancies concentrations, surface termination).
5 The results reported in this work demonstrate that the performance of nitrides related catalyst can
6 be greatly improved upon improving their textural and structural properties.

7

8

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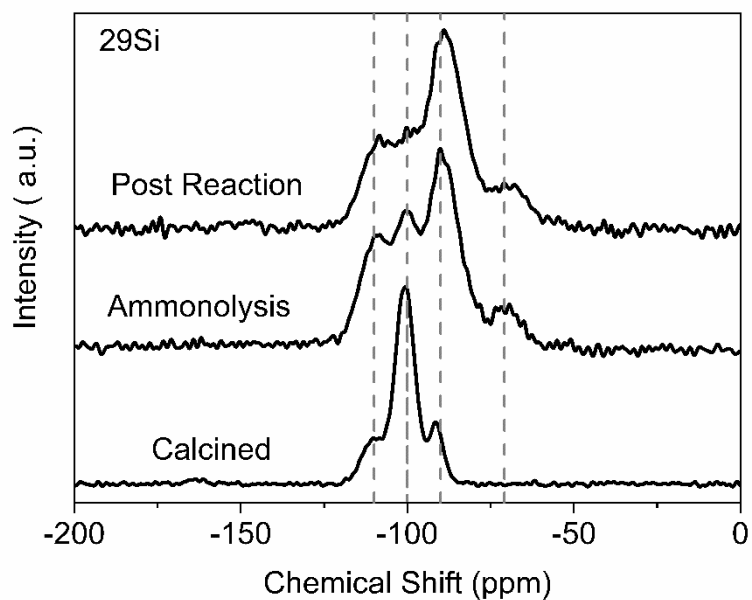
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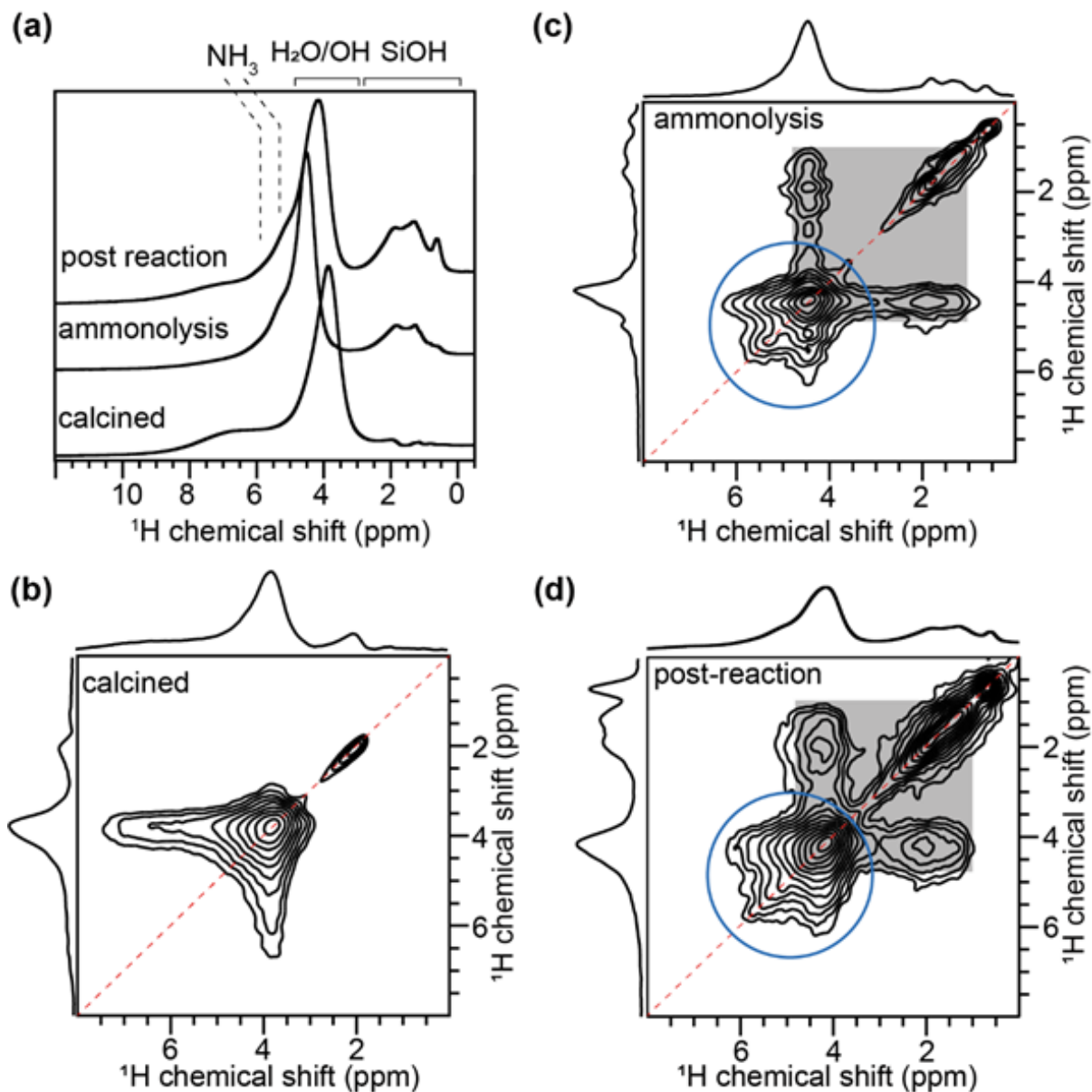
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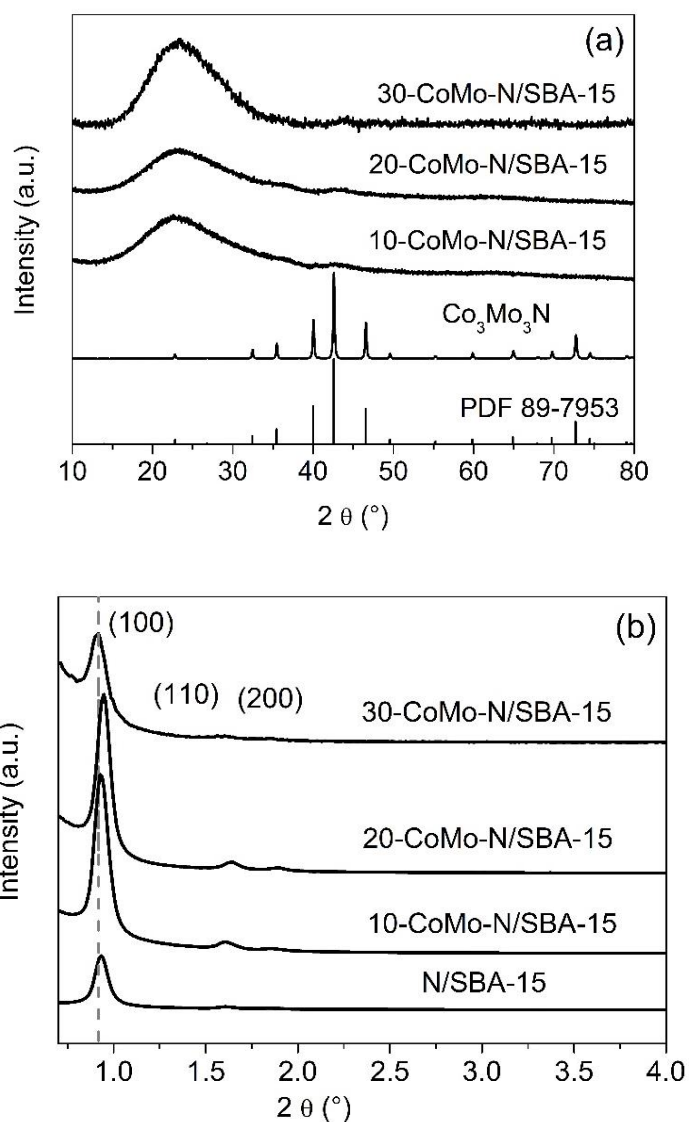
1 **Fig. 1** Solid-state 1D ^{29}Si MAS NMR spectra of (a) calcined SBA-15, (b) after ammonolysis, and
2 (c) after 10h of reaction.



1
 2 **Fig. 2** Solid-state 1D ^1H spectra of SBA-15, ^1H - ^1H 2D NMR spin diffusion spectra of (b) calcined
 3 SBA-15, (c) after ammonolysis, and (d) after 10 h of reaction. For (b-d), the spin diffusion mixing
 4 time was 500 ms. All spectra were acquired at 18.8 T (Larmor frequency of ^1H = 800.1 MHz) with
 5 50 kHz MAS at room temperature.

6

1



2 **Fig. 3** PXR patterns of Co₃Mo₃N and CoMo-N/SBA-15 with different loading. (a) wide-angle
3 PXR and (b) SAXS patterns

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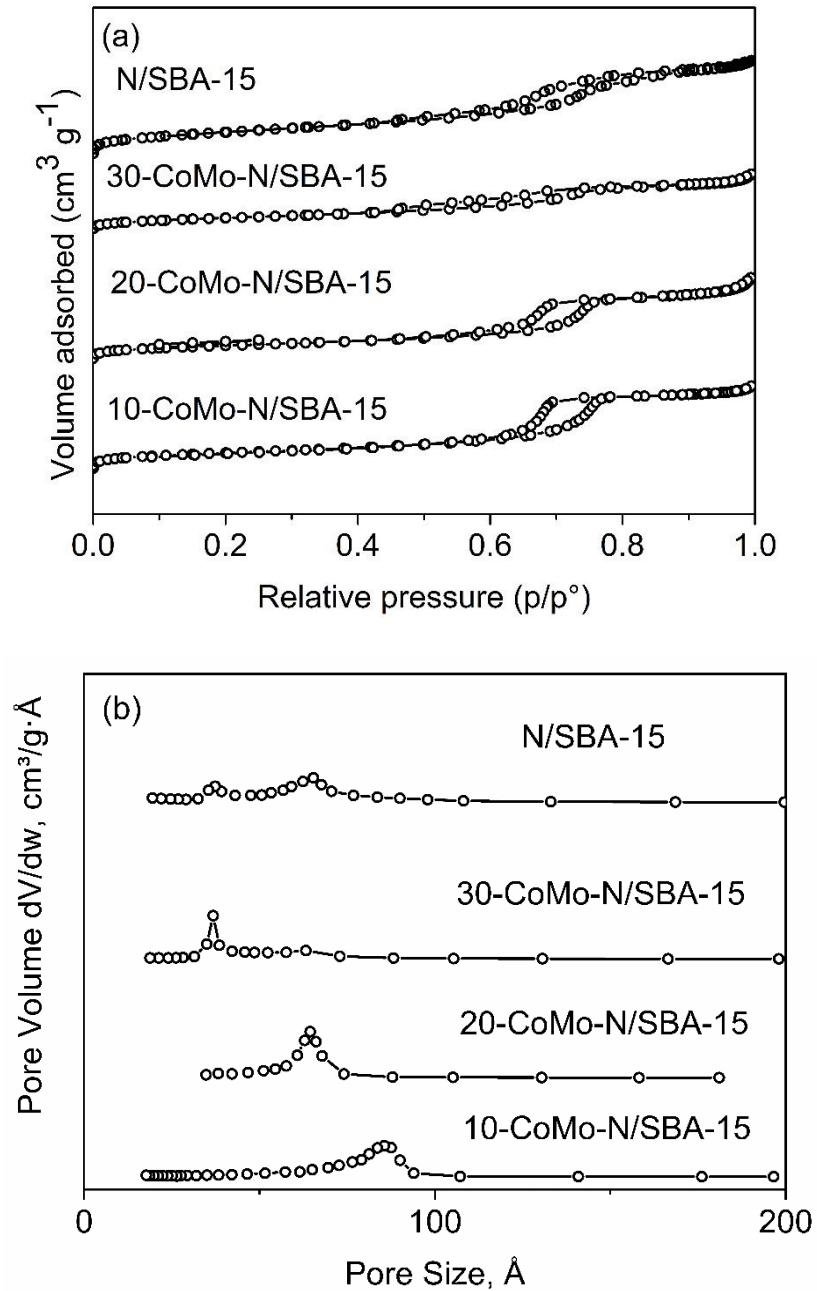
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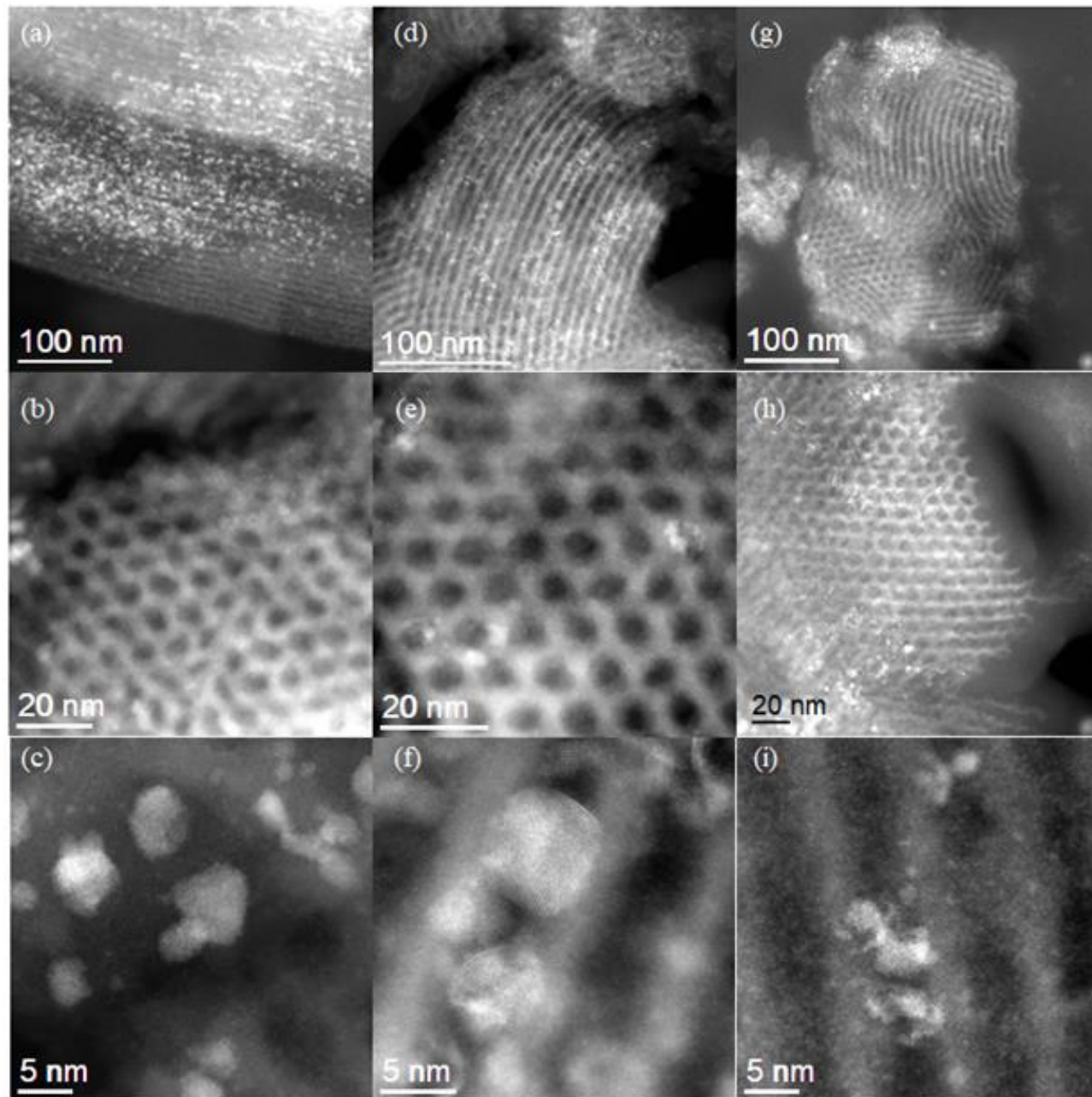


1 **Fig. 4** (a) N_2 adsorption–desorption isotherms and (b) pore size distribution of SBA-15 and
 2 CoMo-N/SBA-15 catalysts after ammonolysis.

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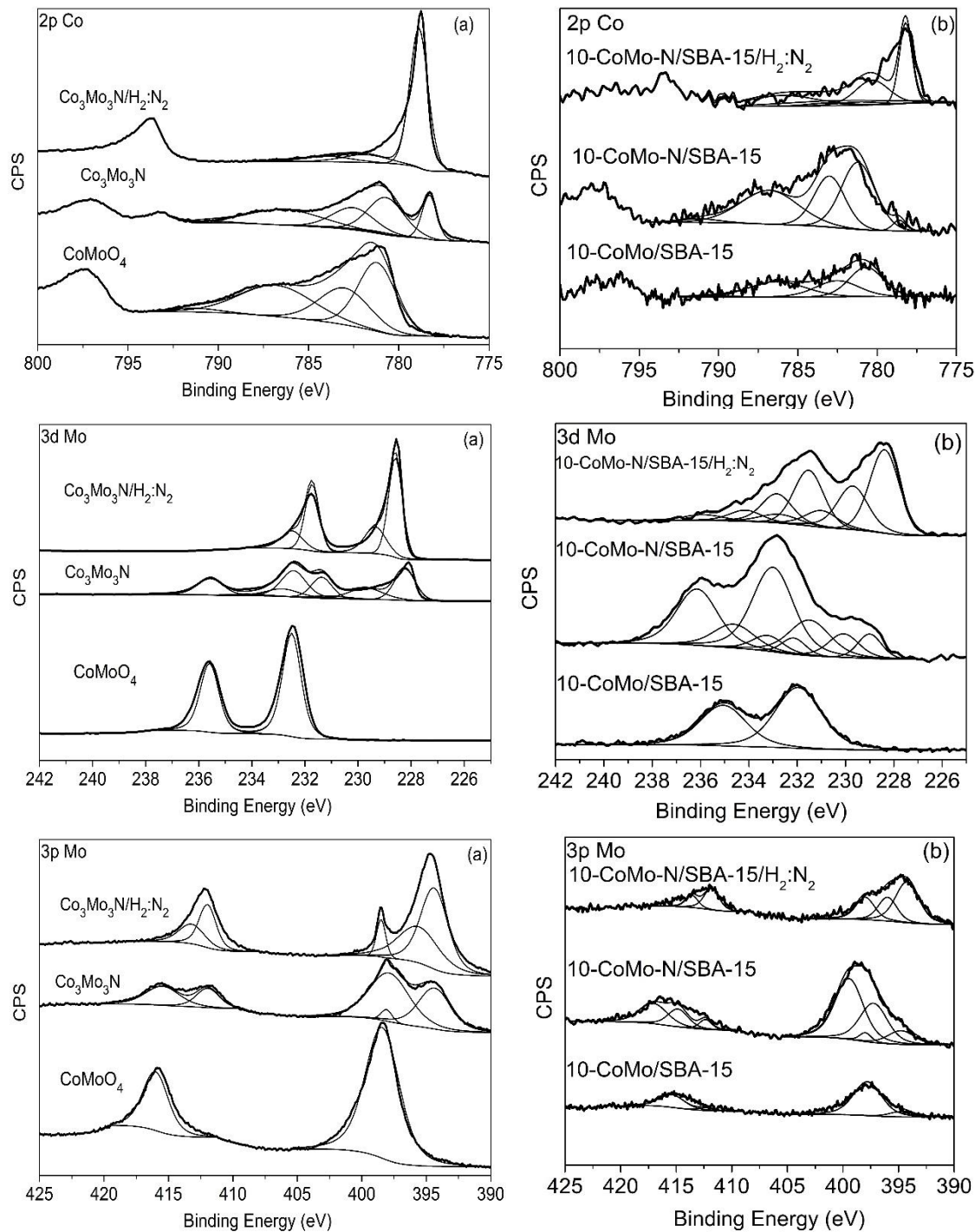
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3 **Fig. 5** Representative HAADF images for supported CoMo/SBA-15 after ammonolysis reaction.
4 10-CoMo-N/SBA-15 (a, b, and c), 20-CoMo-N/SBA-15 (d, e, and f) and 30-CoMo-N-SBA-15 (g,
5 h, and i)



1
 2 **Fig. 6** XPS spectra in the Mo 3d region, Co 2p region and Mo 3p region of (a) $\text{Co}_3\text{Mo}_3\text{N}$ and (b)
 3 10-CoMo-N/SBA-15 . $\text{Co}_3\text{Mo}_3\text{N/H}_2:\text{N}_2$ and $10\text{-CoMoN/SBA-15/H}_2:\text{N}_2$ were subject to pre-
 4 treatment under reaction condition at 700°C for 2h in environmental XPS chamber before analysis.

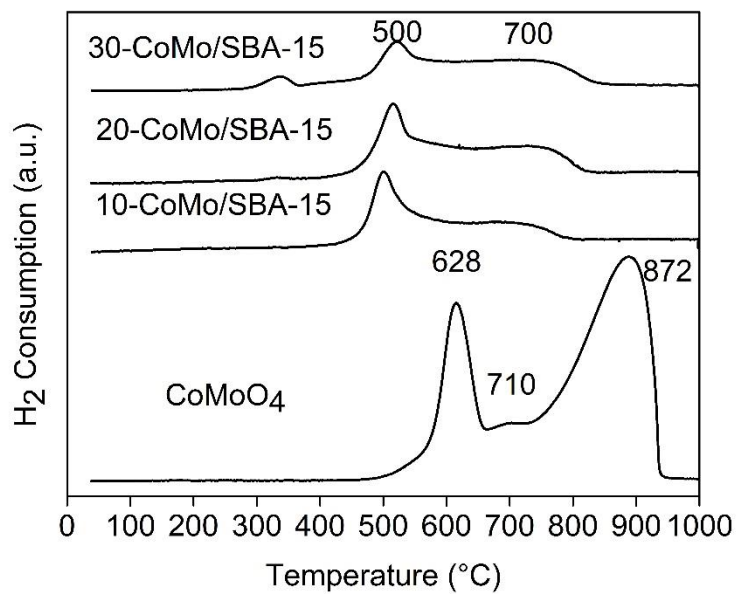
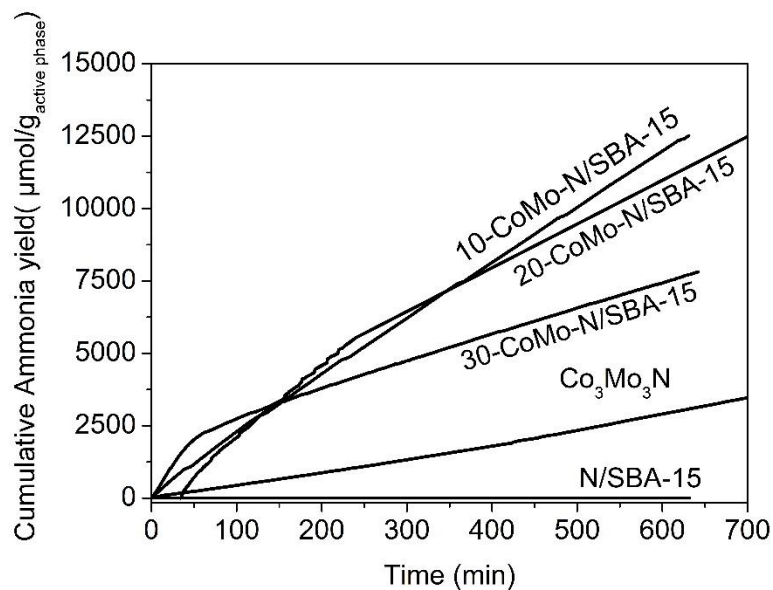


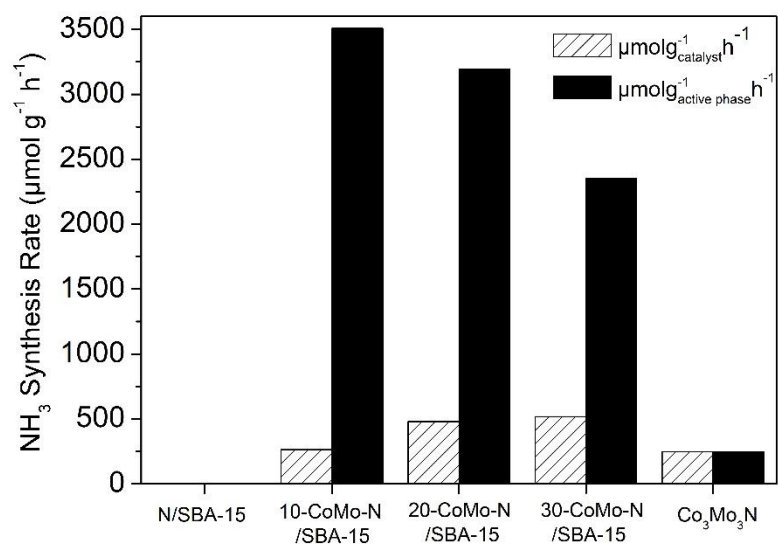
Fig. 7 H₂-TPR profiles of CoMoO₄ and CoMo/SBA-15 catalysts

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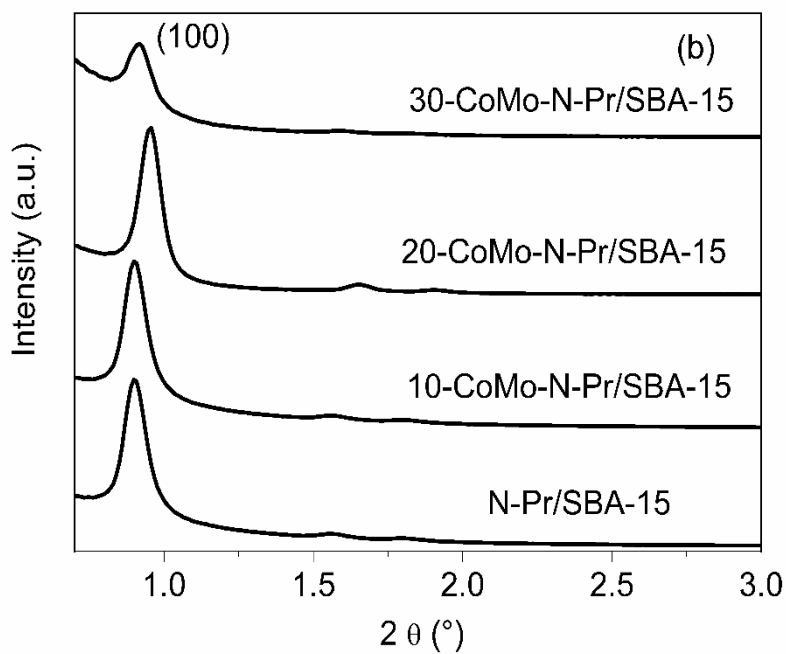
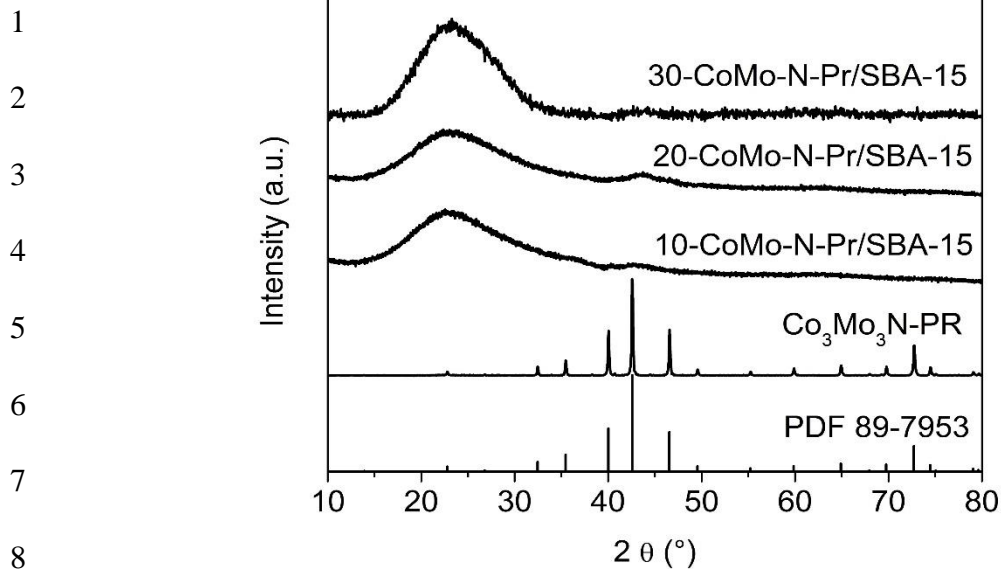
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 2 **Fig. 8** Cumulative ammonia yield obtained of N-SBA-15, Co₃Mo₃N, 10-CoMo-N/SBA-15, 20-CoMo-
 3 N/SBA-15, and 30-CoMo-N/SBA-15. Reaction performed under 60 mL min⁻¹ flow rate of 75 vol.%
 4 H₂/N₂ at 400 °C and ambient pressure.

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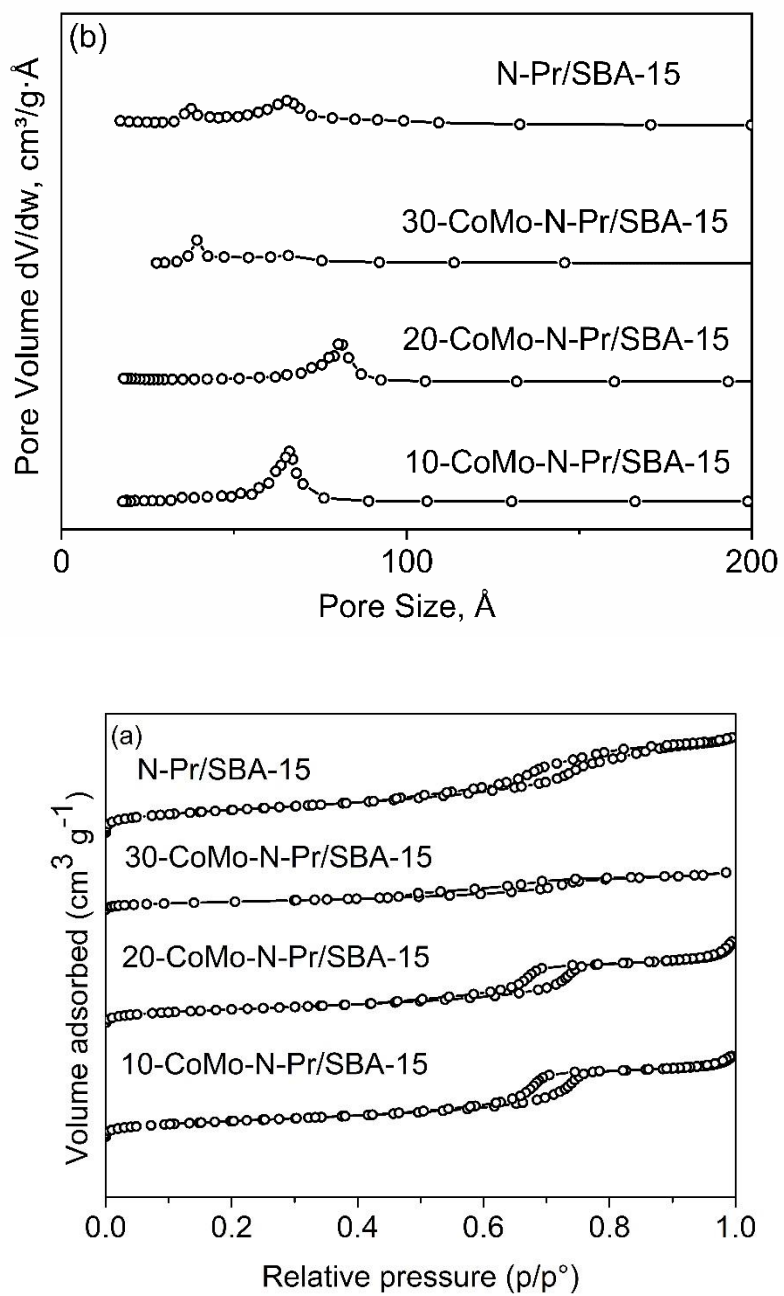


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 2 **Fig. 9** Initial rate of NH₃ synthesis calculated for N-SBA-15, Co₃Mo₃N, 10-CoMo-N/SBA-15, 20-CoMo-
 3 N/SBA-15, and 30-CoMo-N/SBA-15. Reaction performed under 60 mL min⁻¹ flow rate of 75 vol.%
 4 H₂/N₂ at 400 °C and ambient pressure.

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9 **Fig. 10** PXRD patterns of post-reaction Co₃Mo₃N-Pr and CoMo-N-Pr/SBA-15. (a) wide-angle
10 PXRD and (b) SAXS patterns



1
 2 **Fig. 11** (a) N_2 adsorption–desorption isotherms and (b) pore size distribution of post-reaction N-
 3 Pr/SBA-15 and CoMo-N-Pr/SBA-15 catalysts.

1 **Table 1.** Textural properties of SBA-15, unsupported CoMo and supported CoMo-based catalysts
 2 after calcination, ammonolysis and post-reaction.

		$S_{BET},^a$ $m^2.g^{-1}$	$S_{\mu},^b$ $m^2.g^{-1}$	$V_p,^c$ $cm^3.g^{-1}$	$V_{\mu},^d$ $cm^3.g^{-1}$	$D_p,^e$ nm	$a_0,^f$ nm	$t_0,^g$ nm
CoMoO₄	After calcination	6.1	-	-	-	-	-	-
Co₃Mo₃N	After ammonolysis	13.0	-	-	-	-	-	-
	Post-reaction	8.6	-	-	-	-	-	-
SBA-15	After calcination	760	131	1.12	0.06	6.5	11.48	4.98
	After ammonolysis	504	9.6	0.75	-	6.1	10.92	4.82
	Post-reaction	526	19.3	0.82	-	6.1	10.89	4.79
10-CoMo-N/SBA-15	After calcination	390	50	0.71	0.02	7.1	11.11	4.01
	After ammonolysis	348	19	0.71	0.005	6.8	10.87	4.07
	Post-reaction	376	-	0.65	-	6.9	11.35	4.45
20-CoMo-N/SBA-15	After calcination	344	44	0.64	0.02	7.2	10.99	3.79
	After ammonolysis	361	14.4	0.70	-	7.6	10.76	3.16
	Post-reaction	359	9.3	0.61	-	6	10.65	4.65
30-CoMo-N/SBA-15	After calcination	295	44	0.43	0.02	5.8	11.35	5.55
	After ammonolysis	285	14	0.49	-	5.8	11.11	5.31
	Post-reaction	213	4	0.35	-	5.7	11.11	5.41

3 ^a S_{BET} Calculated by the BET method; ^b S_{μ} microporous surface area; ^c V_p total pore volume calculated using
 4 BJH method; ^d V_{μ} micropore volume; ^e D_p mean pore size calculated using B.J.H method, ^f lattice parameter
 5 calculated by hexagonal structure and bragg's equation, ^g wall thickness, $a_0 - D_p$

1 **Table 2.** Summary of the catalytic activity of CoMo-N/SBA-15 catalysts in the ammonia synthesis
 2 under 60 mL min⁻¹ of 75 % H₂ in N₂ (BOC, 99.98 %) at 400 °C and atmospheric pressure.

	Mo/Co atomic ratio*	Initial rate		Stationary rate**	
		μmol g _{catalyst} ⁻¹ h ⁻¹	μmol g _{active phase} ⁻¹ h ⁻¹	μmol g _{catalyst} ⁻¹ h ⁻¹	μmol g _{active phase} ⁻¹ h ⁻¹
SBA-15	0	0	0	0	0
Co₃Mo₃N	0.99	248	248	259	259
10-CoMo-N/SBA-15	1.088	263	3507	120	1714
20-CoMo-N/SBA-15	0.796	479	3193	200	1429
30-CoMo-N/SBA-15	0.386	518	2355	170	810

3 * ratio calculated from TEM/EDS quantification

4 ** Ammonia synthesis rate calculated after reaching steady state condition

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1 ***Credit authorship contribution statement***

2 **Amanda Sfeir:** Investigation, Formal analysis, Validation, Writing Original Draft; **Camila A.**
3 **Teles:** Formal analysis, Investigation; **Carmen Ciotonea:** Review & Editing; **G. N. Manjunatha**
4 **Reddy:** Formal analysis, Investigation; **Maya Marinova:** Formal analysis, Investigation ; **Jérémy**
5 **Dhainaut :** Review & Editing; **Axel Löfberg:** Supervision, Writing - Review & Editing; **Jean-**
6 **Philippe Dacquin:** Supervision, Conceptualization, Formal analysis, Writing - Review & Editing.
7 **Sébastien Royer:** Supervision, Conceptualization, Funding acquisition, Formal analysis, Writing
8 - Review & Editing; **Said Laassiri:** Supervision, Conceptualization, Funding acquisition, Formal
9 analysis, Writing - Review & Editing.

10

11 **Declaration of Competing Interest**

12 The authors declare that they have no known competing financial interests or personal relationships
13 that could have appeared to influence the work reported in this paper.

14

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Supplementary information

**Enhancing ammonia catalytic production over spatially
confined cobalt molybdenum nitride nanoparticles in SBA-15**

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Marinova³, Jérémy Dhainaut,¹ Axel Löfberg,¹ Jean-Philippe Dacquin¹, Sébastien Royer^{1*}, Said
Laassiri^{4*}

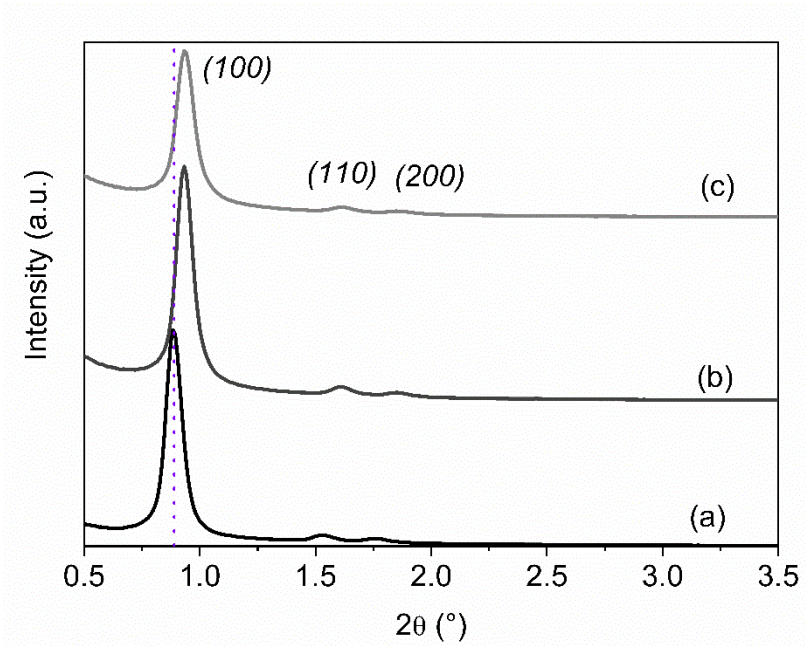
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1 **Fig. S1** SAXS diffractogram of SBA-15 (a) after calcination, (b) after ammonolysis, and (c) after
2 ammonia synthesis reaction.

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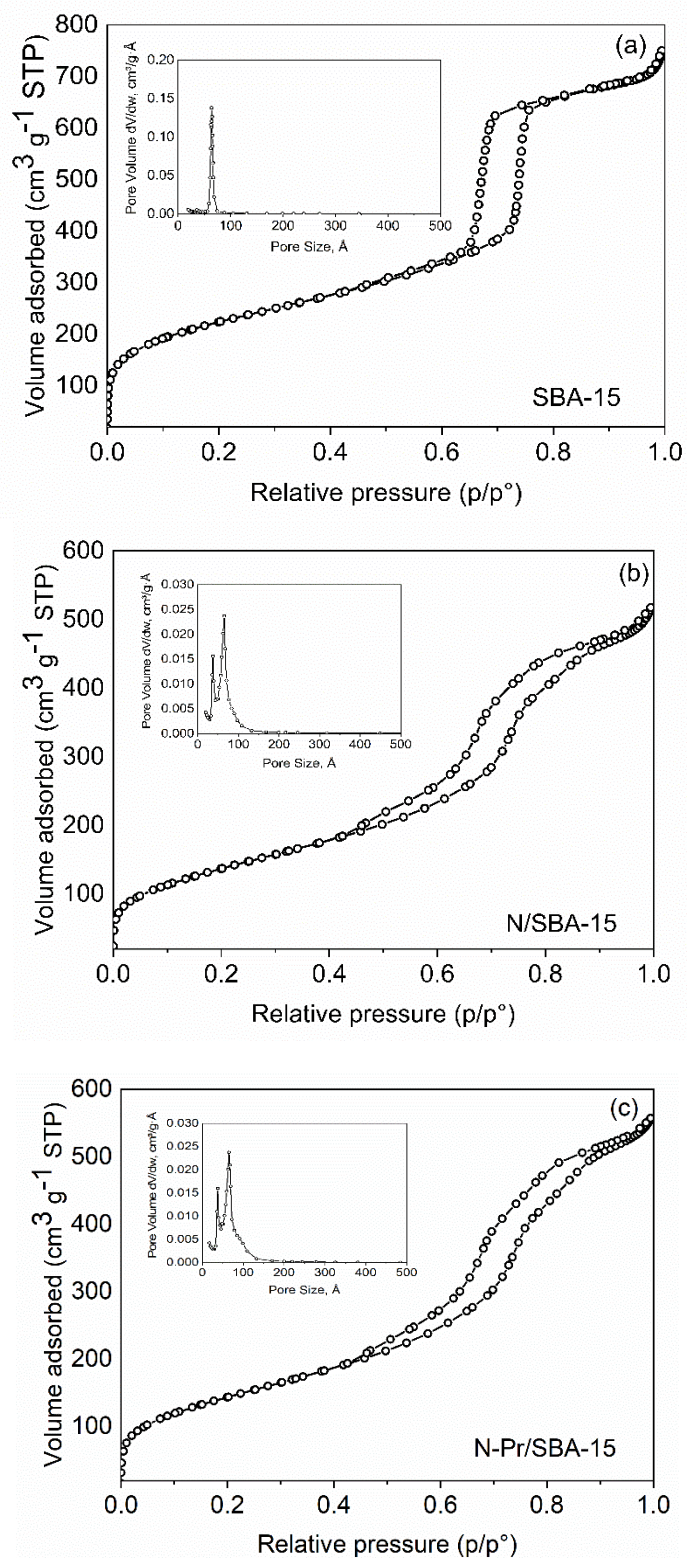
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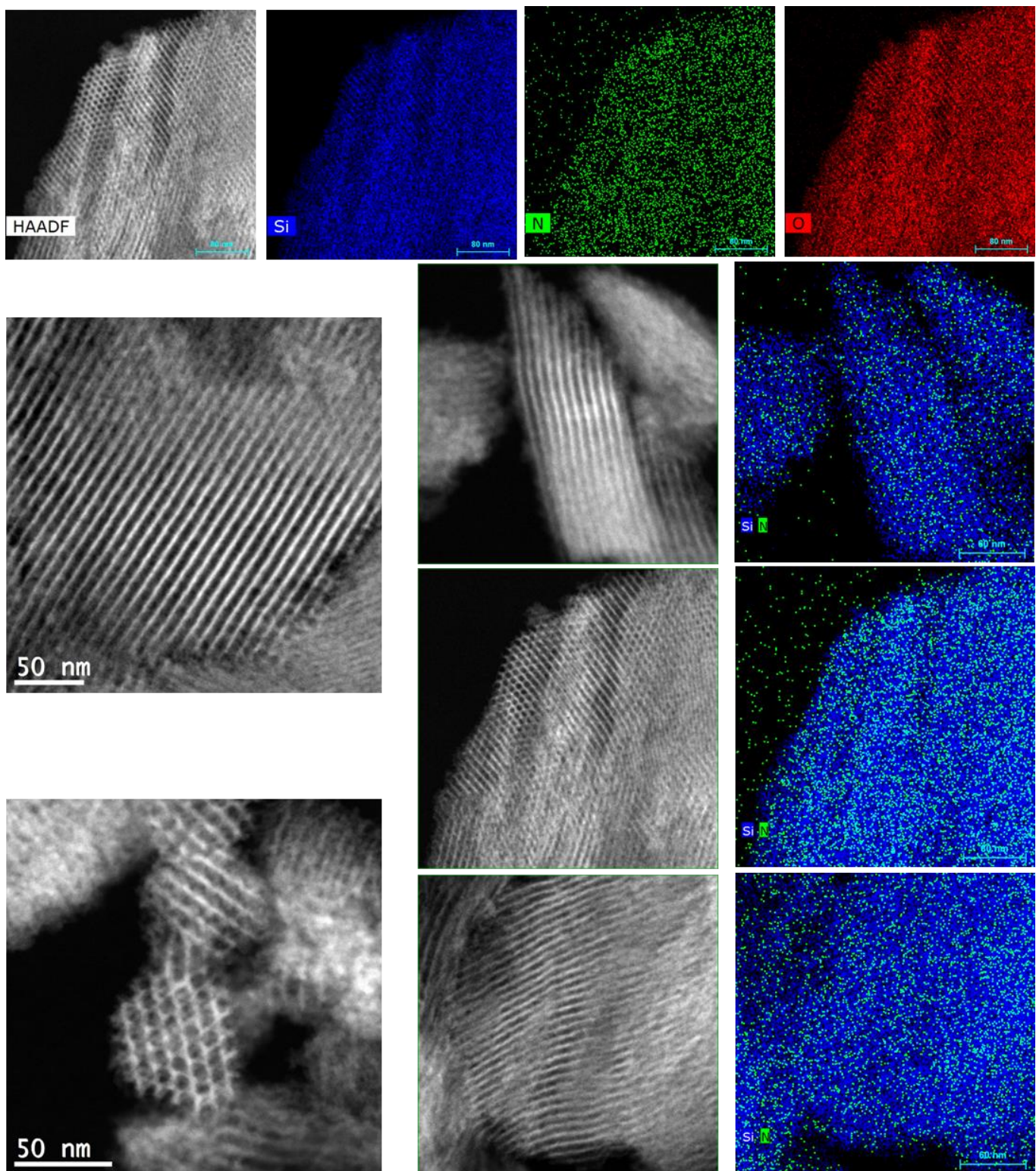
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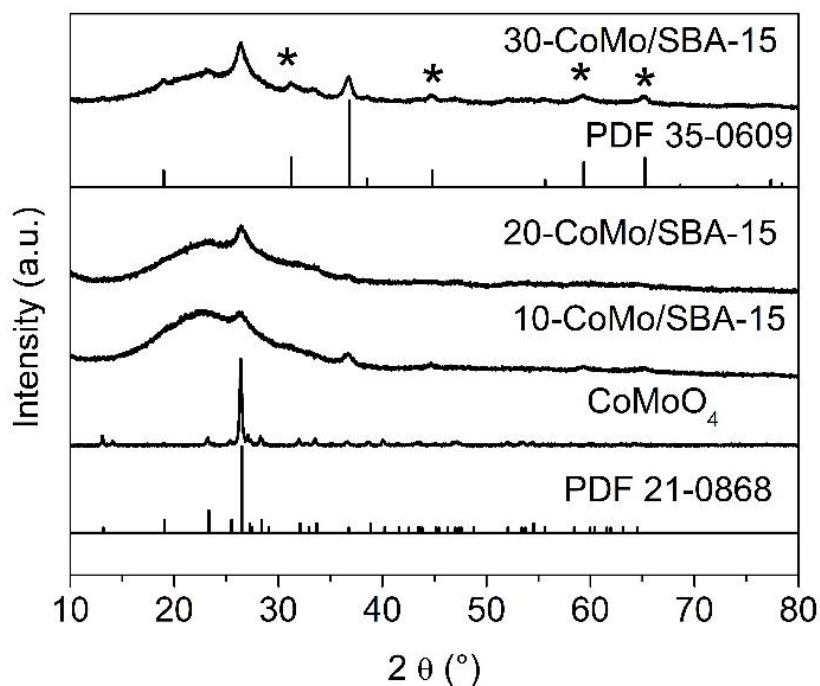
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1 **Fig. S2** N_2 adsorption/desorption isotherms and pore size distribution of SBA-15. (a) after
 2 calcination, (b) N/SBA-15: after ammonolysis, and (c) N-Pr/SBA-15: post-reaction.



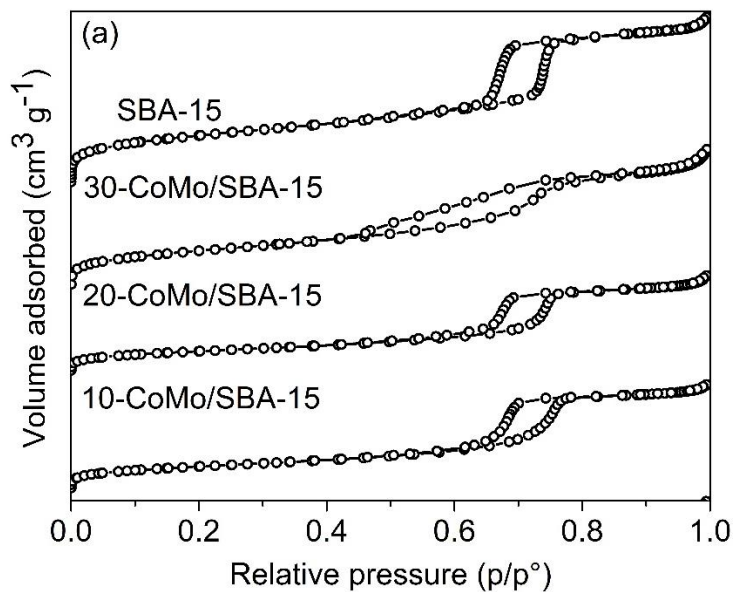
1 **Fig. S3** Representatives HAADF micrograph of N/SBA-15 coupled with EDS for chemical
 2 analysis



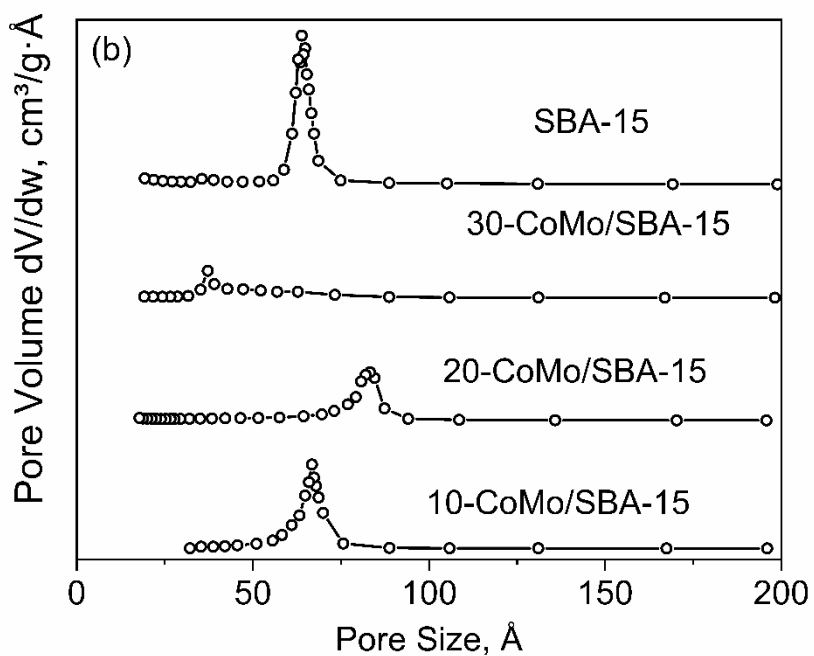
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 2 **Fig. S4** Wide angle PXRD patterns of CoMoO₄ and supported CoMo/SBA-15 with different
 3 loading after the calcination step
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 5 For all the supported materials, a typical broad XRD peak of amorphous silica at $2\theta \sim 24^\circ$ is
 6 observed. In addition to the characteristic XRD signature of SBA-15, an XRD reflection peak at
 7 $2\theta \sim 26^\circ$ that can be attributed to CoMoO₄ phase is also detected for all CoMo/SBA-15 loadings
 8 (10, 20 and 30 wt.%). The low intensity of these peaks suggests that the CoMoO₄ phase is well
 9 dispersed over the support. However, at high CoMo loading (30-CoMo/SBA-15), additional XRD
 10 diffraction peaks appear at $2\theta \sim 31.3^\circ$, 36.8° , and 44.8° . These peaks are characteristic of a Co₃O₄
 11 spinel phase (PDF 35-0609) indicating phase segregation.

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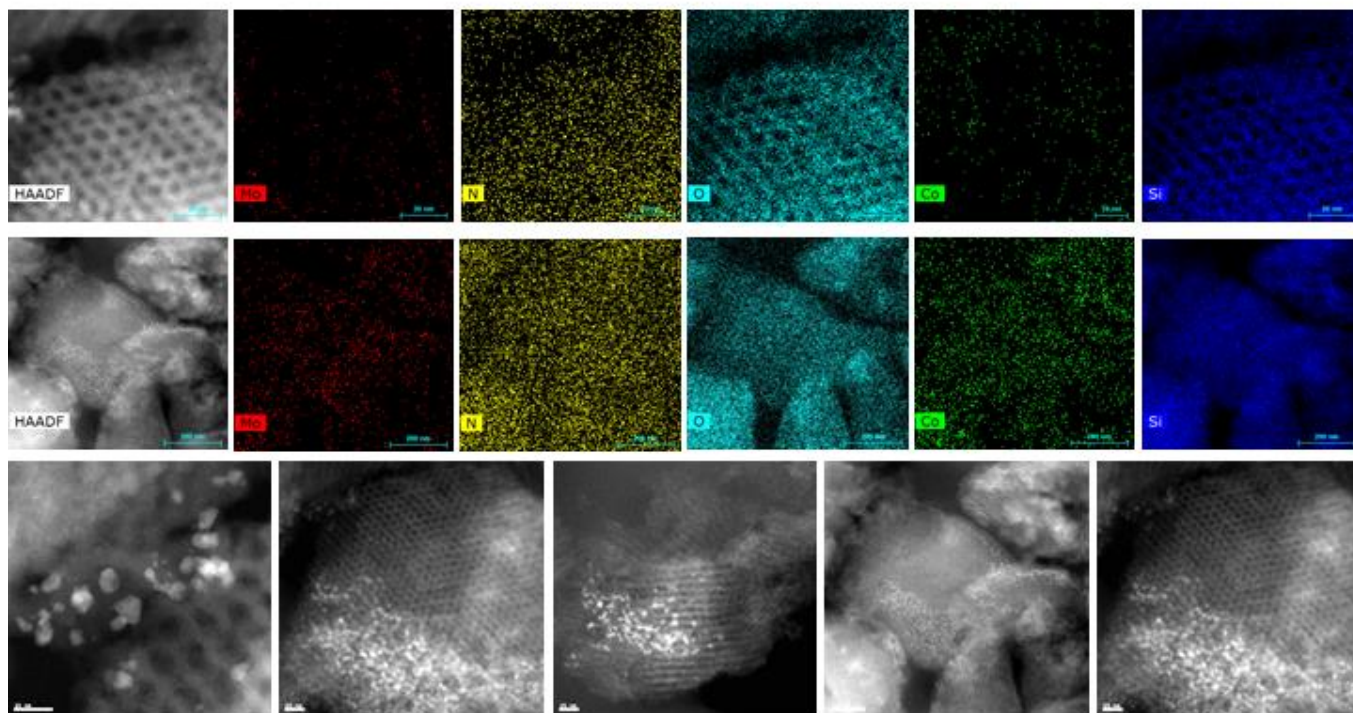


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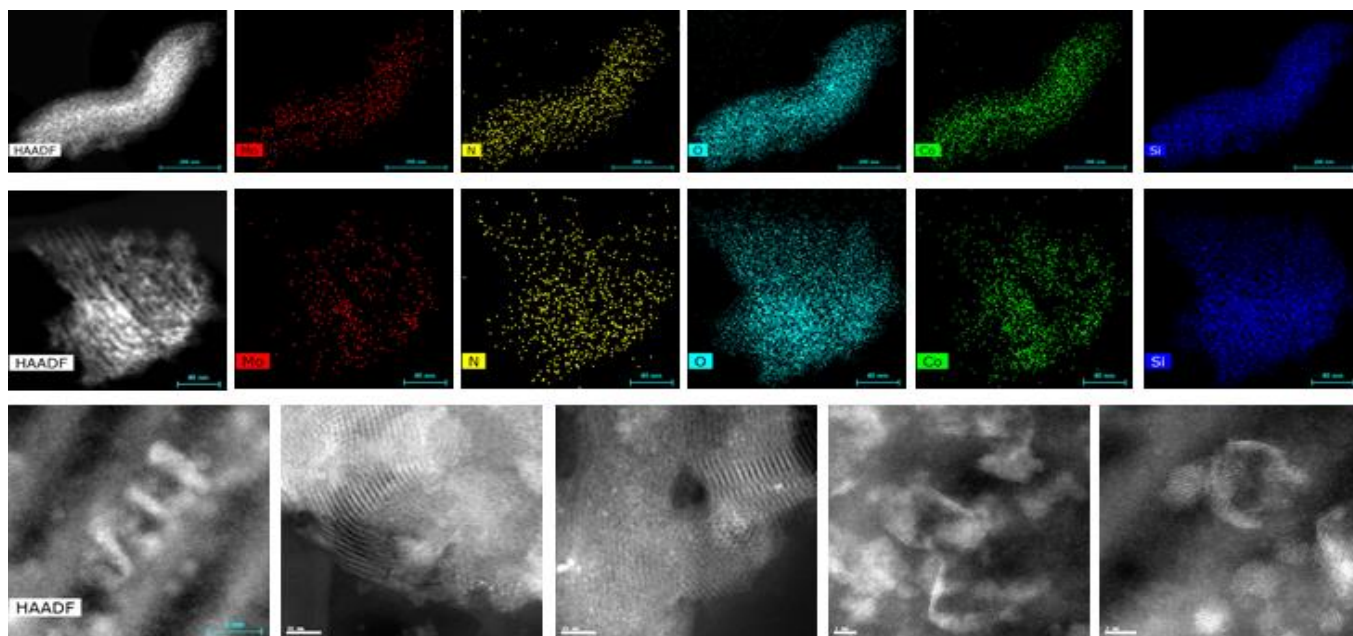


4 **Fig. S5** (a) N₂ adsorption/desorption isotherms and (b) pore size distribution of SBA-15 and
5 CoMo/SBA-15 catalysts with different amounts of metal loading after the calcination step

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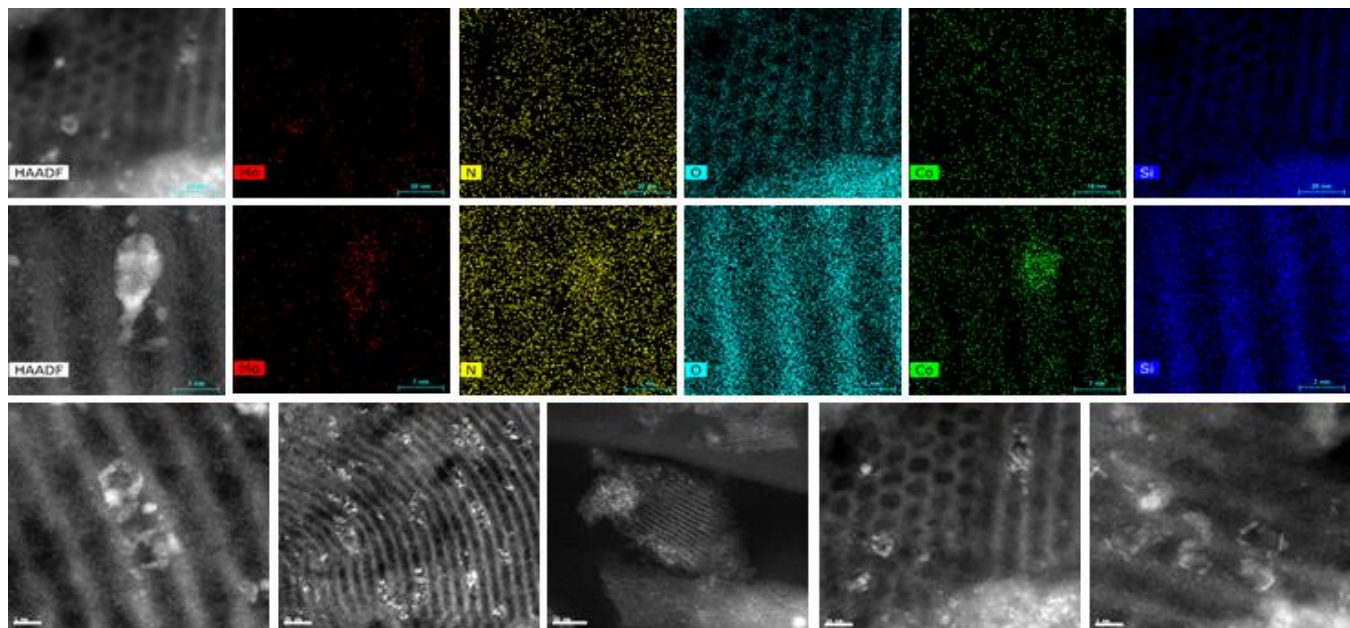


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 2 **Fig. S6-a** representatives HAADF-STEM micrograph of 10-CoMo-N/SBA15 coupled with EDX
 3 for chemical analysis



4 **Fig. S6-b** representatives HAADF-STEM micrograph of 20-CoMo-N/SBA15 coupled with EDX
 5 for chemical analysis

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2 **Fig. S6-c** representatives HAADF-STEM micrograph of 30-CoMo-N/SBA15 coupled with EDX
3 for chemical analysis
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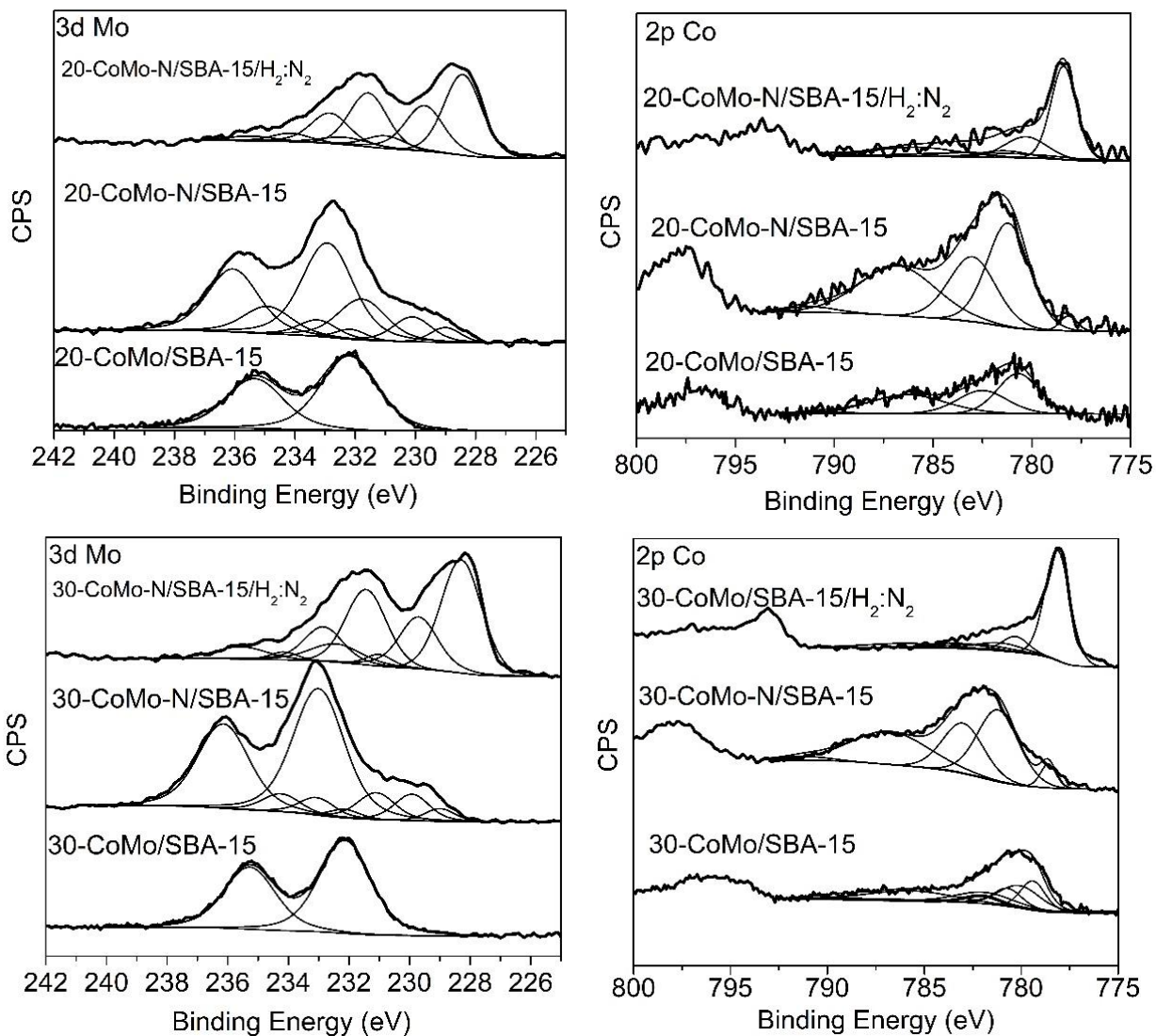


Fig. S7 High resolution XPS spectra in the Mo 3d region and Co 2p region for 20-CoMo/SBA-15 and 30-CoMo/SBA-15

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1 **Table S1.** Position of Mo peaks of unsupported and supported CoMo-N/SBA-15 at different
 2 synthesis steps

	Mo Peaks								Surface Composition			
	Mo ⁶⁺		Mo ⁵⁺		Mo ⁴⁺		Mo-N		Mo ⁶⁺	Mo ⁵⁺	Mo ⁴⁺	Mo-N
	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}	(%)	(%)	(%)	(%)
CoMoO ₄	232.50	235.60	-	-	-	-	-	-	100	-	-	-
Co ₃ Mo ₃ N	232.43	235.57	231.00	234.14	229.70	232.84	228.23	231.37	38.64	5.35	22.52	33.49
Co ₃ Mo ₃ N-PT*			-	-	229.35	232.49	228.59	231.73		-	32.82	67.18
10-CoMo/SBA-15	232.96	235.10	-	-	-	-	-	-	100	-	-	-
10-CoMo-N/SBA-15	233.00	236.14	231.49	234.63	230.08	233.22	229.00	232.14	56.35	23.69	11.77	8.19
10-CoMo-N/SBA-15*	232.74	235.88	231.00	234.14	229.70	232.84	228.38	231.52	7.74	12.32	30.58	49.36
20-CoMo/SBA-15	232.20	235.35	-	-	-	-	-	-	100	-	-	-
20-CoMo-N/SBA-15	232.92	236.06	231.77	234.91	230.1	233.24	229.00	232.14	59.27	24.28	11.66	4.79
20-CoMo-N/SBA-15*	232.43	235.57	231.00	234.14	229.7	232.84	228.29	231.43	12.99	4.3	27.5	55.21
30-CoMo/SBA-15	232.13	235.27	-	-	-	-	-	-	100	-	-	-
30-CoMo-N/SBA-15	233.00	236.40	231.10	234.24	229.92	233.06	229.0	232.14	74.21	11.55	10.46	3.78
30-CoMo-N/SBA-15*	232.43	235.57	231.00	234.14	229.7	232.84	228.29	231.43	12.98	4.29	27.5	55.23

3 * catalyst subject to pre-treatment under reaction condition at 700°C for 2h in environmental XPS chamber before
 4 analysis

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1 **Table S2.** Position of Co peaks of unsupported and supported CoMo nitride materials at each
 2 synthesis step

	Co peaks							Surface composition	
	Co ²⁺ 2p _{3/2}	Co ²⁺ 2p _{3/2}	Co ²⁺ 2p _{3/2}	Co ²⁺ 2p _{3/2}	Co-N 2p _{3/2}	Co-N 2p _{3/2}	Co-N 2p _{3/2}	Co ²⁺ (%)	Co-N (%)
CoMoO ₄	781.20	783.00	786.79	791.19	-	-	-	100	-
Co ₃ Mo ₃ N	780.71	782.51	786.30	790.70	778.30	781.30	783.30	81.58	18.43
Co ₃ Mo ₃ N-PT*					778.88	781.88	783.88		100
10-CoMo/SBA-15	780.7	782.50	786.29	790.69	-	-	-	100	-
10-CoMo-N/SBA-15	781.20	783.0	786.79	791.19	778.60	781.60	783.60	97.25	2.75
10-CoMo-N/SBA-15*	780.30	782.10	785.89	790.29	778.26	781.26	783.26	50.2	49.8
20-CoMo/SBA-15	780.7	782.50	786.29	790.69	-	-	-	100	-
20-CoMo-N/SBA-15	781.20	783.0	786.79	791.19	778.15	781.15	783.15	97.49	2.51
20-CoMo-N/SBA-15*	780.30	782.10	785.89	790.29	778.39	781.39	783.39	44.62	55.38
30-CoMo/SBA-15	780.1	781.9	785.69	790.09	-	-	-	57.99**	-
30-CoMo-N/SBA-15	781.20	783.0	786.79	791.19	778.60	781.60	783.60	94.39	5.61
30-CoMo-N/SBA-15*	780.30	782.10	785.89	790.29	778.13	781.13	783.13	24.12	75.88

3 * catalyst subject to pre-treatment under reaction condition at 700°C for 2h in environmental XPS chamber before
 4 analysis

5 ** 42.0% of the surface composition of Co was in the form of Co₃O₄

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Table S3. Reducibility of CoMo/SBA-15

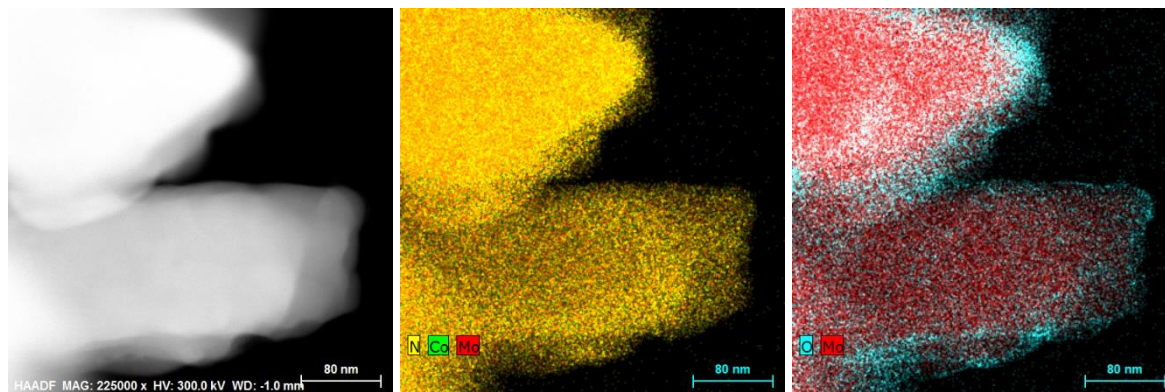
Catalyst	H₂ consumption (mmol/g)
CoMoO ₄	13.72
10-CoMo/SBA-15	2.18
20-CoMo/SBA-15	2.95
30-CoMo/SBA-15	5.05

1 **Table S4.** d spacing and corresponding hkl planes observed by TEM coupled with FFT on 10-
 2 CoMo-N/SBA-15 upon 48 h of reaction with 60 mL.min⁻¹ of a 5% H₂/Ar mixture at 400°C and
 3 ambient pressure

d- spacing (Å) observed	d- spacing (Å) standard*	2 θ	I fix	(h k l)
2.38	2.3880	37.637	811	(1 1 0)
2.30	2.30028	39.130	7	(1 1 3)
2.03	2.03408	44.506	462	(0 1 11)
1.90	1.91857	47.344	293	(2 0 5)
1.20	1.19400	80.353	177	(2 2 0)

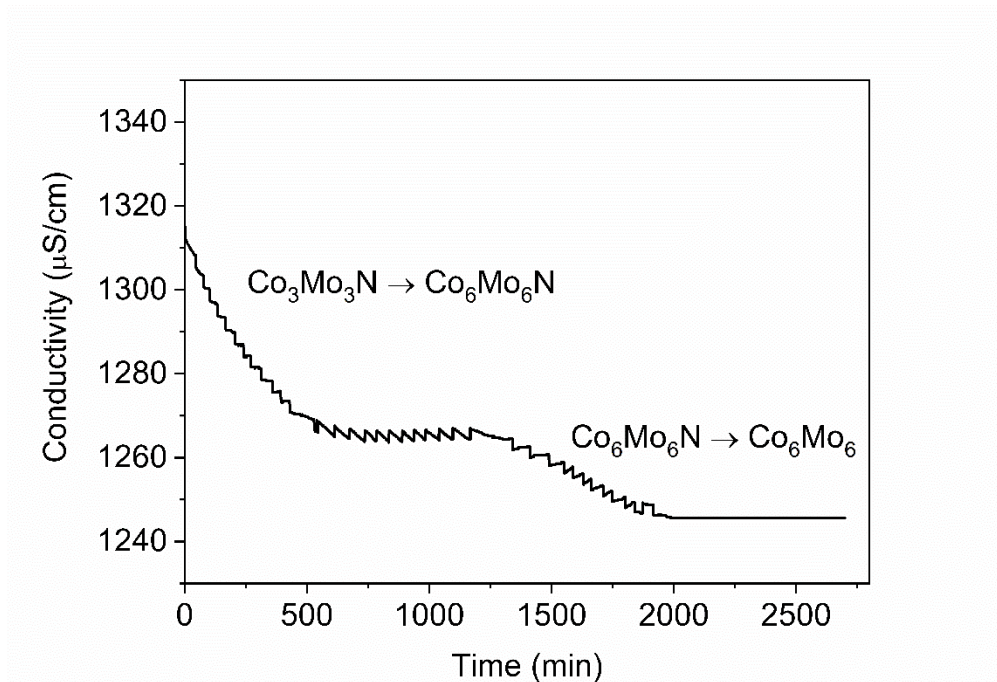
4 * intermetallic Mo_{6.25}Co_{6.75} (PDF number: 04-018-9512)

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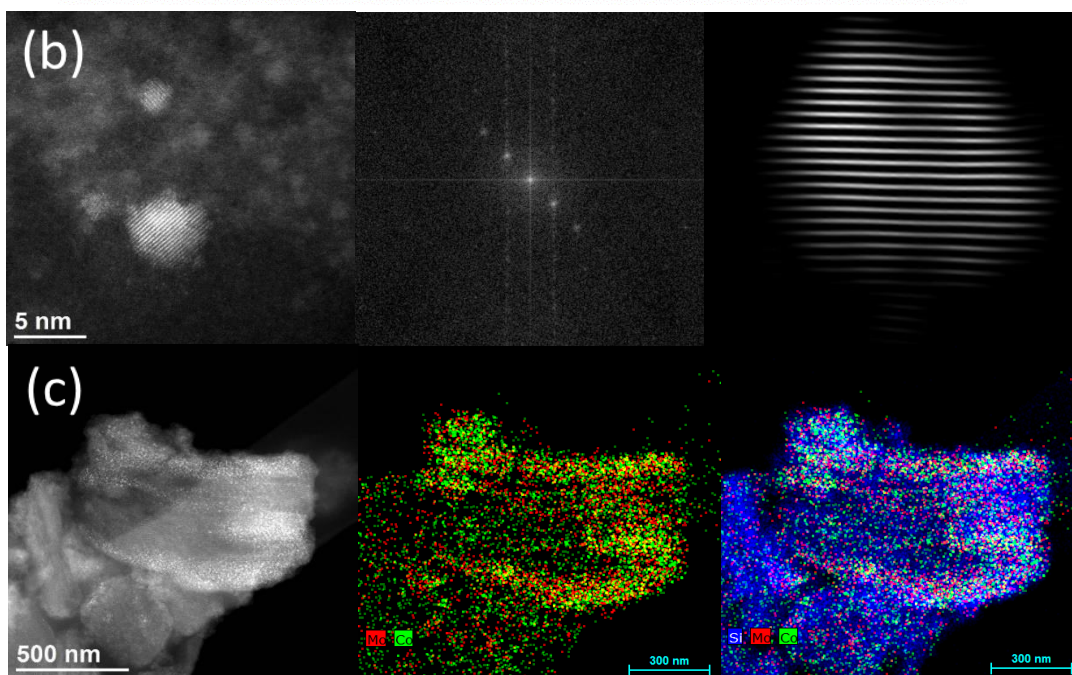
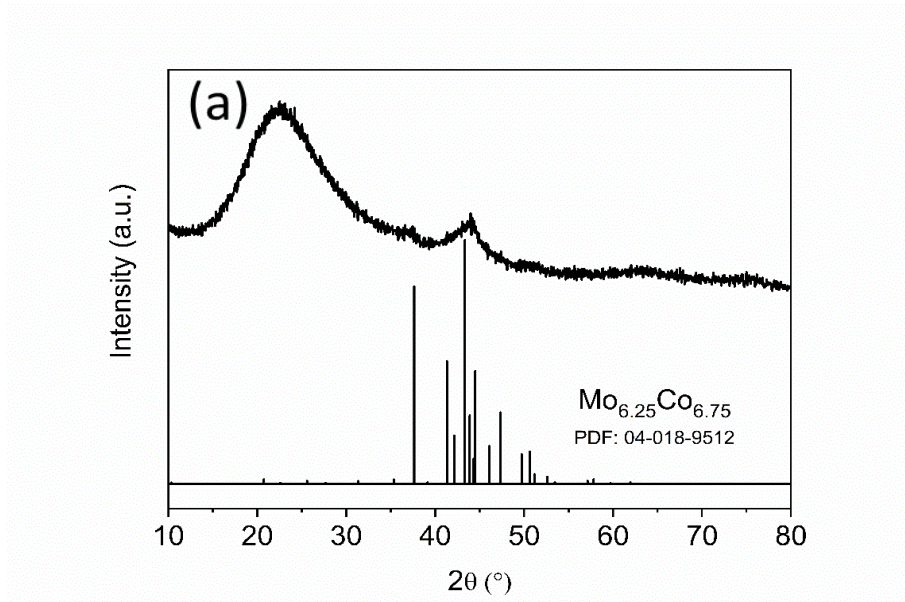
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2 **Fig. S8** Representative HAADF-STEM micrographs of $\text{Co}_3\text{Mo}_3\text{N}$ coupled with EDS for elemental
3 analysis (Light blue: O ; Green: Co ; Yellow: N ; Red: Mo)

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2 **Fig. S9** Ammonia production rate of 10-CoMo-N/SBA-15 reacted with $60 \text{ mL}\cdot\text{min}^{-1}$ of a 5%
3 H_2/Ar mixture at 400°C and ambient pressure

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 2 **Fig. S10** Post-reaction catalyst 10-CoMo-N/SBA-15 after 48 h of reaction with 60 mL.min⁻¹ of a
 3 5% H₂/Ar mixture at 400°C and ambient pressure (a) XRD pattern (b) FFT image indicating the
 4 (1 1 0) plane (c) HAADF image coupled with EDS
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