Active and stable Fe-based catalyst, mechanism, and key role of alkali promoters in ammonia synthesis.#

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#: Dedicated to the memory of Yves Chauvin

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Highlights

- Cs and K impact drastically the Fe NPs dispersed on N-C support material toward ammonia synthesis.
- A core-shell structure of the Fe NPs obtained with Fe⁽⁰⁾ located on core and surrounded by Cs or K oxides.
- The DFT reveals a geometrical repartition of alkali, leading to a larger number of exposed iron atoms.
- A non-dissociative mechanism proposed by DFT, a stepwise addition of H on N leading to NH₃.

Abstract: Worldwide NH₃ production reached 0.18 Gton in 2019, and 1-2 % of the global CO₂ emissions are due to large-scale NH₃ synthesis (1 billion tons of CO₂ / year). A catalyst for ammonia synthesis has been obtained by pyrolysis of iron phthalocyanine (FePc) precursor under N₂, followed by impregnation with alkali metals (Na, Li, K, and Cs) and H₂ treatment. Characterization (XPS, XRD, HR-TEM, ICP-OES, TGA, CHNS analysis, and BET) revealed nano-sized core-shell structures formed during H₂ treatment, with Fe in the core and

promoters ("Cs₂O" and "K₂O") with carbon on the shell. The alkali metals partially inhibit the methanation process of carbon. These Fe NPs were found to be very active and stable catalysts, as compared to the commercial iron-based catalyst KM1 (Haldor-Topsoe). Activities of promoted catalysts follow the order: K>Cs>Na~Li, with more than 6% of NH₃ at 400 °C and 7 MPa, and contact time (WHSV) of 12000 ml.g⁻¹.h⁻¹ with K. The apparent activation energy was found to be 31 kJ.mol⁻¹ and 34 kJ.mol⁻¹ for 3-K-FePc₇₀₀ and 10-Cs-FePc₇₀₀ suggesting the facile activation of N₂ on the catalysts surface. DFT-based predicted atomic and electronic structures reveal a similarity in the partial charge distribution on surface Fe species with K or Cs. Surprisingly the main effect of alkali is related to the geometrical repartition of alkali, leading to a larger number of exposed iron atoms, active sites, in the case of K than Cs. The alkali (present as metal oxide) leaves at medium coverage of the surface some exposed Fe⁽⁰⁾ for N₂ non-dissociative chemisorption (end-on type). The free energy profile demonstrates that the thermodynamic stability of the reaction intermediates for nitrogen reduction reaction (NRR) increases with pressure indicating better feasibility of the reaction at higher pressures.

Keywords: *Ammonia synthesis, Iron phthalocyanines, Non-dissociative mechanism, Alkali promoters, Electronic and geometrical effects.*

Abbreviations: *Iron phthalocyanine: FePc; Supporting Information: SI; X-ray diffraction: XRD; Inductively Coupled Plasma-Optical Emission Spectrometry: ICP-OES; Gas hourly space velocity: WHSV; Mass Spectrometer: MS; X-ray photoelectron spectroscopy: XPS; Temperature-programmed reduction: Temperature-programmed reduction: TPR; Thermogravimetric analysis: TGA; Time on stream: TOS.*

1. Introduction

Ammonia is one of the largest-volume industrial chemicals synthesized in the world, owing to the use of NH₃ as the source of most fertilizers for agriculture, various nitrogen-containing chemicals and materials, nitric acid, clean-burning fuels, refrigerant fluid, and H₂ storage and distribution as a significant energy carrier of the future.[1-5] However, the enormous negative environmental impact of the Haber-Bosch process, contributing 1-2 % of the global CO₂ emissions, urgently requires the development of more active and more stable catalysts based on cheap metals for ammonia synthesis.[6-8]

Commonly used catalysts for this process are based on iron, cobalt, or ruthenium with alkali promoters in their formulations.[9-11] The alkali metals are usually reported as "electronic promoters", although important surface structural effects have also been claimed to be due to the addition of these alkali metals.[12, 13] The alkali promotion is commonly assumed to proceed via "electron transfer" from the alkali to the Fe or Ru surface.[14-16] As a result, the barrier for

“nitrogen dissociation” would be decreased. Indeed, some authors claim “nitrogen dissociation” is the rate-limiting step in ammonia synthesis.[10, 17-20] In parallel, all NH_x species, including adsorbed NH_3 molecule, would be destabilized, resulting in more “vacant sites” on the active surface and thus increasing the catalytic activity.[21, 22][23, 24] Other authors point out that the addition of alkali metals would remove the so-called “retarding” species ($\equiv\text{N}$, $=\text{NH}$, $-\text{NH}_2$) from the surface. In this theory, the surfaces of Fe catalysts are believed to be covered by the intermediate surface NH_x species, which are in equilibrium with the produced ammonia and the reactant hydrogen. Highly negative order with respect to NH_3 (about -2 reported for most of the iron-based catalysts) indicates that the “retarding species” ($\equiv\text{N}$, $=\text{NH}$, and $-\text{NH}_2$) are strongly adsorbed to the surface. In this context, the surface nature of the catalyst might be drastically changed by the addition of alkali, changing the relative concentration of the main surface adsorbed species ($-\text{NH}_3$, $-\text{NH}_2$, $=\text{NH}$, and $\equiv\text{N}$).[25]

Even though dissociated forms of dinitrogen are likely formed on the surface during ammonia synthesis, their role in the mechanism of ammonia synthesis is not proven. A non-dissociative mechanism has been recently proposed in which the adsorbed N_2 undergoes systematic hydrogenation to $^*\text{HNNH}$, $^*\text{NH-NH}_3$, and $\text{NH}_{3(g)}$. [18, 26, 27] The mechanistic hypotheses are based on experimental and DFT calculations, showing that a single Ta atom on silica surface transforms N_2 to ammonia by a non-dissociative mechanism. Other examples performed by DFT calculations lead to the same conclusions with Fe_3 cluster on the $\theta\text{-Al}_2\text{O}_3(010)$ surface single-atom catalysis.[28, 29]

Very efficient and stable catalysts for ammonia synthesis have been recently developed in our laboratory based on the pyrolysis of FePc.[30] The same material was also claimed to be precursors for the reverse reaction of ammonia decomposition to H_2 and N_2 . [31]

In general, the solid-state pyrolysis of metal-organic compounds (e.g., MOFs or phthalocyanines) generates metal NPs confined into carbon porous nanostructures.[32-34] The material resulting from pyrolysis of FePc, which are iron NPs supported on nitrogen-doped carbon composites, exhibit catalytic activities for ammonia synthesis and compare favourably with benchmark industrial iron catalysts (iron doubly promoted catalyst, KM1 from Haldor Topsoe) when combined with alkali metals.[30, 35] The important role of the alkali metal in these systems was illustrated by the fact that in the absence of the alkali metal, the reaction rate was dramatically decreased. [36, 37] Thus, we found it exciting to elucidate the real effect of the alkali metal in the recently developed phthalocyanine-based catalysts for ammonia synthesis for Fe-based catalysts.[30] [38]

Scheme 1. Schematic illustration for the preparation of promoted FePc catalysts towards ammonia synthesis.

The catalyst was prepared via two steps: firstly, pyrolysis under nitrogen of the FePc precursor at high temperature and secondly, activation/reduction under a hydrogen atmosphere at 525 °C (**Scheme 1**). Herein, we decided to elucidate the role of various promoters on the structure of the catalyst. However, we could not do this investigation without elucidating the structural modifications occurring during these two steps (pyrolysis and H₂ treatment) of synthesis. The objective was to obtain a structure-activity relationship in a complex system. For that purpose, many techniques were systematically applied. The critical role of the alkali metals (especially K and Cs) on the ammonia synthesis (localization on the surface and chemical composition) has been clearly identified. Furthermore, using DFT calculations, we predict the structure of the catalysts, particularly after the addition of K and Cs and their role in improving the catalytic activity of the catalysts. The final core-shell structures with Fe in the core and carbon-alkali metal in the shell results in high catalytic activity attributed to the intimate contact of the alkali with the active species, providing at the same time structure stability by preventing the methanation and ensuring the iron dispersion, as well as controlling the exposed active area by the geometric repartition of the alkali species on the catalytic structure.

2. Experimental Section

2.1. Synthesis:

Several catalysts were studied with the aim of understanding the structural transformations occurring during the 2 steps involved in the preparation of the catalysts derived from phthalocyanine starting materials (pyrolysis under N₂ followed by H₂ treatment) and the role of the alkali metal in the catalytic performance of FePc catalysts for ammonia synthesis reaction. Experimental procedures are detailed in supporting information (SI).

The iron-based catalysts were prepared by the pyrolysis of FePc. The FePc precursor was introduced onto a crucible and heated (2 °C/min) under nitrogen flow (100 ml/min) to different

temperatures ranging from 600 to 800 °C and kept for 3 h. After cooling down to room temperature, the materials were passivated under 5% O₂ in N₂ for one hour. After pyrolysis, alkali metal (Li, Na, K, Cs) nitrates were incorporated by incipient impregnation using a water-ethanol mixture (2/1 vol. ratio). Before the catalytic test, an activation/reduction step under H₂ was carried out at 525 °C for 6 h. Finally, the samples were kept under an inert atmosphere inside a glove box.

In order to analyze the effect of pyrolysis temperature, several samples were prepared at different pyrolysis temperatures in the range of 600-800 °C. These materials were named FePc_x, where **x** (600, 700, and 800 °C) indicates the pyrolysis temperature. After pyrolysis, those samples were impregnated in the open air with 10% wt. Cs and finally reduced under H₂ at 525 °C for 6 h, before activity measurement. In the particular case of Cs, the catalysts were named **10-Cs-FePc_x**.

In order to analyze the effect of the promoters on structure and activity, different alkalis (Li, Na, K, Cs,) were incorporated in the FePc material obtained after pyrolysis at 700 °C, keeping constant the molar content 0.77 mmol/g of material after pyrolysis. The samples were named **Y**, with **Y** (Li, Na, K, Cs) indicates the alkali impregnated on FePc₇₀₀. For example, for Li the sample was named **Li-FePc_x**.

2.2. Catalytic test:

The catalytic performance to evaluate the activity in ammonia synthesis reaction was studied in a fixed-bed flow reactor using Micro activity units, PID. The catalytic activity for all the catalysts was evaluated at 400 °C and different pressure in the range 0.1-7 MPa; and the stability of the catalytic performance versus time on stream at 7 MPa and 400 °C. Constant volume of the catalyst (0.25 mL, ~200 mg or 0.125 mL, ~100 mg) and reactant mixture flow rate (N₂/H₂, 1/3, 40mL/min), was used to keep constant gas hourly space velocity (WHSV) of 12000 or 24000 ml g⁻¹ h⁻¹. Before the catalytic tests, the pretreatment or activation steps were carried out under H₂/N₂ (3/1 molar ratio) at 490 °C for 6 h. In order to avoid any contact with the open air, the catalyst was loaded into the reactor inside the glovebox, where the catalysts are kept after the activation treatment under hydrogen. This protocol was developed to take into consideration for rate measurements the weight loss that occurs during this reduction treatment (analyzed and described below). This provided accurate ammonia synthesis rates expressed in μmol NH₃ h⁻¹g_{cat}⁻¹ as well as ammonia % in the reactor outlet. The NH₃ produced in each experiment was monitored quantitatively by an online connected Mass-Vac Spectrometer (detection limit less than 5 ppb). See more details in SI.

2.3. Computational Methodology:

For Fe support simulation, we considered the (4 x 4) cubic periodic slab model containing 5 Fe layers or 160 atoms from the optimized bulk cell dimensions of the body-centered cubic (bcc) crystal structure by cleaving the original bulk through a matrix transformation along with the (110) Miller index crystallographic plane to obtain the required surface. We set a relatively large vacuum width in the perpendicular direction to the surface to avoid any fictitious interaction between the neighboring slabs along this direction. We have chosen this number of Fe layers after performing benchmark convergence tests on the evolution of the electronic structure features (such as cohesive energy and Fermi level position) as a function of the slab thickness.

For simulations of Cs- and K- containing Fe structures, (Cs₂O)_n and (K₂O)_n clusters (n= 2, 3, and 4) with O : Cs and O : K ratios of 0.5 were deposited on top of Fe(110) surface to mimic the obtained experimental samples by maintaining +1 oxidation states for Cs and K species. Several possible key atomic structures for the clusters, particularly for n = 4, revealing aggregated (symmetric or distorted) and dispersed geometry types, were explored in order to find the most favorable situations of Cs and K species on top of Fe(110) surface. For n = 3 and 2, the lowest-energy structures were found starting successively from the most stable configurations obtained for n = 4. They were obtained by removing, respectively, one and two Cs₂O (or K₂O) species from different structural locations on the Fe surface to ensure the convergence of the minimum electronic energy.

All generated geometries were optimized by means of the periodic density functional theory (DFT) with the projector augmented plane wave (PAW) method [39] as implemented in the VASP simulation software.[40-43] The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [44] together with a kinetic energy cutoff of 400 eV for electron wave basis functions, and a 3 x 3 x 1 Monkhorst-Pack *k*-point grid for sampling the first Brillouin zone were used.[45] The valence electrons taken into account explicitly in the PAW potentials are 3d⁷4s¹ for Fe, 5s²5p⁶6s¹ for Cs, 3s²3p⁶4s¹ for K, and 2s²2p⁴ for O. The spatial positions of the various species were fully relaxed and the structures were considered well converged when the three principal residual Hellmann–Feynman forces on each species were near 0.01 eV.Å⁻¹, the atomic displacements were near 10⁻⁴ Å, and the convergence criterion for the self-consistent field (SCF) cycles for energy change was near 0.01 meV. Thermodynamic calculations were performed to estimate the most stable catalyst structures by mimicking the experimental setup used for preparation. The considered reaction used H₂ in the gas phase as a hydrogen source as follows:

The formation of energy was computed using this expression: $E_{\text{form}}(1) = E[\text{Fe}(110)\text{-A}_{2n}] - E[\text{Fe}(110) - (\text{A}_2\text{O})_n] + n \cdot E[\text{H}_2\text{O}] - n \cdot E[\text{H}_2] + n \cdot \Delta\mu_{\text{H}_2\text{O}} - 2n \cdot \Delta\mu_{\text{H}}$ (2).

The electronic energies of $\text{Fe}(110)\text{-(A}_2\text{O)}_n$ and $\text{Fe}(110)\text{-A}_{2n}$ materials in their lowest-energy configuration were described by $E[\text{Fe}(110) - (\text{A}_2\text{O})_n]$ and $E[\text{Fe}(110) - \text{A}_{2n}]$. $E[\text{H}_2\text{O}]$ and $E[\text{H}_2]$ represent the electronic energies of H_2O and H_2 molecules in gas phase. The thermal part of hydrogen or water chemical potential ($\Delta\mu_{\text{H}}$) or ($\Delta\mu_{\text{H}_2\text{O}}$) depends on temperature (T) and partial pressure (p) through the enthalpy (h) and entropy (s) corrections. The zero-point vibrational energy as a function of T and p was included into the thermal corrections. This was computed through DMol software [46] within the PBE functional and the double numerical polarization (DNP) basis set. [47] Here, $\Delta\mu_{\text{H}}$ was varied as a function of $p(\text{H}_2)$ under the experimental condition $T = 400$ °C. $\Delta\mu_{\text{H}_2\text{O}}$ was fixed at the same temperature and at atmospheric pressure. For $\text{Fe}(110) - (\text{A}_2\text{O})_n$, the reference formation energy was set to 0 eV to compare relatively the stability of $\text{Fe}(110) - \text{A}_{2n}$ catalysts to the pristine ones. This methodology has demonstrated its capability of matching the experimental observations while studying the thermodynamics of doped or defective materials used in catalysis and photoelectrochemistry. [48-50]

Bader charge analysis was performed on the most stable structures to give deep insight into any possible electron transfer between the deposited alkali Cs and K elements and the Fe support. This analysis was also helpful in identifying the species involved in this process as well as the amount of transferred electrons.

3. Results and Discussion

3.1. Structural Characterization:

3.1.1. Pyrolysis temperature

Several catalysts were prepared at different pyrolysis temperatures in the range of 600-800 °C (First step, **Scheme 1**). Structural transformation occurring during the pyrolysis has been investigated by TGA, XRD, XPS, elemental analysis CHNS, ICP-OES, N_2 physisorption. Results are detailed in the SI (**Figs. S2-S5 and Table S1**). During the pyrolysis step, the decomposition of the organic ligand provokes changes in the structure and composition (Fe, C, and N) of the material. Carbon and nitrogen contents decrease, and a simultaneous iron content increase is observed with increasing pyrolysis temperature. After the pyrolysis step of FePc at different temperatures (600-800 °C), 10 % wt. of Cs was introduced (0.077 mol%/g). The samples were activated under pure H_2 at 525 °C for 6 h (**Scheme 1**) to obtain the catalysts (10-Cs-FePc₆₀₀, 10-

Cs-FePc₇₀₀, and 10-Cs-FePc₈₀₀) that were kept in a glove box. The activation process under the hydrogen atmosphere is required to form the catalytically active α -Fe species. [51, 52]

Reducibility of the iron species and changes in the structure and composition occurring during the activation has been investigated by TPR, TGA, XRD, ICP-OES, CHNS, and BET (**Figs. S6-S7 and Table S2**). Interestingly, the reduction of iron occurs together with incomplete hydrogenation of the carbon support to form methane.[53-55] This methanation process of the carbon support results in a considerable weight loss of the sample, corresponding decrease of the carbon content (55-60 wt. %) and an increase in the iron content while providing mesoporosity to the final material (pore size > 2 nm). A significant loss of nitrogen content is also observed. The XRD patterns of 10-Cs-FePc₆₀₀ and 10-Cs-FePc₇₀₀ catalysts (**Fig. S7**) show that the materials undergo various phase transformations during the H₂ treatment 525 °C, to form mostly α -Fe as evidenced by the reflections of α -Fe, 110, 200, and 211, at 44.7°, 65.0°, and 82.3° (2 θ), respectively.

The morphology of the catalysts after activation under H₂ at 525 °C for 6 h was imaged by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Representative TEM images, their corresponding elemental mapping (Fe, Cs, C, and O), and the particle size distribution for 10-Cs-FePc₆₀₀, 10-Cs-FePc₇₀₀, and 10-Cs-FePc₈₀₀ are illustrated in **Fig. 1 and Fig. S9 A**. The TEM images show a population of spherical iron nanoparticles supported homogeneously onto the nitrogen-doped carbon with a fainter contrast corresponding to a cesium layer decorating the surface of the iron nanoparticles.

The pyrolysis temperature strongly affects the particle size distribution of the metallic iron nanoparticles, with an increase in the average particle size from 12 to 70 nm, when increasing the pyrolysis temperature at 600 °C, 700 °C, or 800 °C (**Fig. S9 A**).

Interestingly, the elemental map of the catalysts confirmed the formation of a core-shell structure, with the Fe located in the core, whereas the Cs, C, and O were distributed on the shell (**Fig. 1 B, D, and F**). More specifically, the line scan analysis across the NPs (**Fig. 1, D, and G**) explored under Argon inert atmosphere clearly shows that Cs and O atoms are forming an amorphous “Cs_xO” phase dispersed around the Fe NPs. Furthermore, with HR-TEM imaging (**Fig. 1 H**), we can see clearly that the carbon and alkali metals are forming a multilayer structure in the shell without a possible distinction between Cs and C. Moreover, at the interface of iron and carbon, there is a possibility to have an iron-carbide; nevertheless, it is difficult to identify by XPS or XRD. Note also that the modeling studies regarding the possible reduction of the “Cs₂O” phase indicate that Cs(*1) cannot be reduced even at elevated temperatures under H₂ (**see later Fig. 8**),

consistent with the XPS analysis. This clearly means that Cs species remains as a cesium oxide within the final material.

The formation of these core-shell structures is claimed to be responsible for the improvement of the activity. Because of this intimate contact between Cs and Fe, a strong metal-promoter interaction is likely to occur and might be the origin of the enhanced catalytic activity. This kind of carbon-shell structure around iron nanoparticles has been previously reported for similar catalysts prepared by pyrolysis of different organometallic compounds, including iron porphyrin precursor. [32, 56]

The surface chemical composition and oxidation state were investigated using XPS of the 10-Cs-FePc₆₀₀, 10-Cs-FePc₇₀₀, and 10-Cs-FePc₈₀₀ after activation under H₂ at 525 °C for 6 h. **Fig. S8** shows that the XPS spectra of the Cs 3d levels exhibit two sharp peaks at 725.1 and 735.2 eV, consistent with Cs⁺¹ oxidation state. [57] While the Fe 2p_{3/2} peaks corresponding to Fe⁽⁰⁾, for the 10-Cs-FePc₆₀₀, 10-Cs-FePc₇₀₀, and 10-Cs-FePc₈₀₀ appeared at ~706.6 eV showing lower intensity (shown in the zoomed area) as compared to the Cs peaks. This corroborates that Cs is covering or is wrapping the iron nanoparticles in agreement with the core-shell structure observed by HR-TEM and HAADF-STEM elemental mapping (**Fig. 1**). A less intense peak at 710.8 eV also appeared in the spectra of 10-Cs-FePc₆₀₀ and 10-Cs-FePc₇₀₀ catalysts, which correspond to iron oxide, whereas in 10-Cs-FePc₈₀₀ catalyst, this peak is not detected. The presence of iron oxide may be due to the experimental pollution of the samples by O₂ present in the introduction chamber, as discussed later.[58]

Fig. 1. HAADF-STEM images for the catalysts after the treatment under H₂ at 525 °C for 6 h; **A:** 10-Cs-FePc₆₀₀, **C:** 10-Cs-FePc₇₀₀, and **E:** 10-Cs-FePc₈₀₀. Elemental mapping computed from spectral imaging data acquired by STEM-EELS; **B:** 10-Cs-FePc₆₀₀ Fe (blue), C (red), and Cs (green); **D:** 10-Cs-FePc₇₀₀ Fe (red), C (dark blue), Cs (green) and O (light blue); **F:** 10-Cs-FePc₈₀₀, Fe (blue), C (red), and Cs (green); **G:** line scan across one of the iron NPs; Fe (red), C (dark blue), Cs (green) and O (light blue), and **H:** HR-TEM picture for 10-Cs-FePc₇₀₀ catalyst.

3.1.2. Various alkali metals

Furthermore, to elucidate the role of the alkali promoters, several catalysts were prepared by using different alkali metals (Li, Na, K, and Cs), while keeping the same molar loading (0.77 mmol/gram). The promoters were introduced after the pyrolysis under N₂ at 700 °C, and the catalysts were then activated under H₂ at 525 °C for 6 h, and finally, kept under an inert

atmosphere, to be analyzed by ICP-OES, CHNS analysis, N₂-Physisorption for BET analysis, XPS, and HR-TEM analysis.

Regarding the composition detailed in **Table 1**, the addition of alkali promoter drastically inhibits the methanation process occurring during the hydrogen treatment. This prevents the sample from the intense weight loss that results in a decrease of the C content and an increase of the Fe content. In the absence of promoter, the amount of C remaining after the reduction process is very low (8 %wt.), and the amount of Fe is very high (80 %wt.). In the presence of promoter, the amount of remaining C is around 32 % wt. and the amount of Fe is around 35 %wt. for 10-Cs-FePc₇₀₀ (**Table 1**).

Therefore, the introduction of alkali metal partially prevents the carbon from interacting with active hydrogen. [54] Note that the weight loss observed during the H₂ treatment leads to a 2 to 3 fold increase in the promoter content compared to the original content (**Table 1**). Notably, after the catalytic reaction, there were no significant changes observed in the alkali content in the catalysts (**Table 1**), suggesting that during the catalytic reaction, the alkali oxide (Cs₂O and K₂O) remains stable.²⁶ At the same time, a slightly smaller loss of N is also observed in the promoted samples (1-2%), compared to the non-promoted one (0.5%) (**Table 1**). It has been claimed that the presence of nitrogen in the catalyst could enhance the catalytic properties of the catalysts. [59, 60] All these values indicate that the alkali metal prevents the loss of carbon, which is becoming the support of Fe NPs. The alkali-promoted samples are mesoporous structures developing a BET surface area range of 80 to 280 m²/g. In contrast, the non-promoted sample had such a low surface area that we couldn't measure it. Indeed, the particle size distribution in FePc₇₀₀ without promoter is higher than 80 nm. [61, 62] The increase in the particle size observed for the non-promoted sample is related to the enormous loss of carbon support (85% weight loss), leading to a final 80 % wt. of Fe content (**Table 1**).

Table 1. Effect of alkali promoter: Composition and textural properties of the catalysts after the H₂ treatment at 525 °C 6 h.

Samples	Fe wt. (%)	^[a] Alkali wt. (%)	Alkali/Fe	C wt. (%)	^[b] N wt. (%)	BET (m ² /g)
FePc ₇₀₀	80	0	0	8	0.5	ND
10-Cs-FePc ₇₀₀	30	23 [22.5]	0.32	32	1	86
3-K-FePc ₇₀₀	43	10 [9.7]	0.33	31	1.5	147
1.8-Na-FePc ₇₀₀	60	6	0.24	22	2	68

0.5-Li-FePc ₇₀₀	51	4	0.63	39	2.1	281
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[a]: the samples were analyzed after a hydrogen treatment at 525 °C, and in the bracket[], the samples were analyzed after the catalytic reaction. [b]: O and H are the remaining elements.

The morphology of 10-Cs-FePc₇₀₀, 1.8-Na-FePc₇₀₀, and 3-K-FePc₇₀₀ catalysts after H₂ treatment at 525 °C were studied by HAADF-STEM images (**Fig. 2**). The Fe NPs are dispersed onto the nitrogen-doped carbon support material, as observed in **Fig. 1**, forming the core-shell structure previously described. The alkali species, Cs, K, and Na, are also distributed over the whole carbon-nitrogen matrix. The iron is located in the core region, whereas the Cs, K, and Na are distributed on the shell mixed with the C and O.

The particle size distribution of 10-Cs-FePc₇₀₀, 3-K-FePc₇₀₀, and 1.8-Na-FePc₇₀₀ catalysts are indicated in **Fig. S9, B**. The 3-K-FePc₇₀₀ and 10-Cs-FePc₇₀₀ give the smaller average particle size (11 and 15 nm, respectively), while larger particles of Fe are observed for 1.8-Na-FePc₇₀₀ (~32.3 nm). The catalyst promoted with all alkali metals (not only Cs) prevents the loss of carbon by inhibiting the methanation, and the iron species remains highly dispersed. It is corroborated that the addition of alkali metals is an important structural promoter to prevent the sintering of the iron nanoparticles.

The XPS analysis for the FePc₇₀₀, 10-Cs-FePc₇₀₀, 3-K-FePc₇₀₀, and 1.8-Na-FePc₇₀₀ catalysts was also investigated. (**Fig. S10**). Surprisingly, for FePc₇₀₀ without a promoter, after reduction under H₂ at 525 °C, the peak around 710.6 eV (iron oxide) is much more intense as compared to the peak of Fe⁽⁰⁾ at 706.6 eV. In contrast, in the case of 10-Cs-FePc₇₀₀, 3-K-FePc₇₀₀, and 1.8-Na-FePc₇₀₀, under identical activation condition, the XPS shows the presence of a sharp peak of Fe⁽⁰⁾ at 706.6 eV and a much smaller intensity peak of iron oxide at 710.2 eV. It can be concluded that the introduction of promoters (Na, K, and Cs) might be beneficial to reduce iron, as also confirmed by the TPR experiment (**Fig. S11**). [57, 63, 64] [52] Regarding the oxidation state, several experiments corroborated a very small amount of iron oxide on 10-Cs-FePc₇₀₀, 3-K-FePc₇₀₀, and 1.8-Na-FePc₇₀₀ catalysts were due to a trace of oxygen impurities in the introduction chamber. To confirm this observation, further XPS experiments were performed and confirmed the absence of this peak (For the details, see SI **Figs. S12–S13**).

Fig. 2. Representative HAADF–STEM images for FePc_{700} without promoter, 10-Cs-FePc_{700} , 3-K-FePc_{700} , and 1.8-Na-FePc_{700} catalysts (After the treatment under H_2 at 525°C for 6 h), and the correspondent elemental mapping: Fe (red), Carbon (blue), Cs, K or Na (green). **A** and **B**: for FePc_{700} without a promoter, **C** and **D**: for 10-Cs-FePc_{700} , **E** and **F**: for 3-K-FePc_{700} , and **G** and **H**: for 1.8-Na-FePc_{700} .

Furthermore, the surface oxidation state was corroborated by the extraction of the Fe branching ratio (L_3/L_2) from a spectrum imaging dataset acquired by STEM –EELS.[65] The computed results (**Fig. 3**) clearly showed about 2 nm thick shell region around the NPs that had a higher branching ratio than the rest of the nanoparticle. [66] This is indicative of a higher valence state for Fe atom located on the surface, which is consistent with the DFT calculations, described later.

Fig. 3. Line-Scan Profile of the Fe branching ratio (L_3/L_2 signals ratio) for 10-Cs-FePc₇₀₀ catalyst (After activation under H₂ at 525 °C for 6 h).

3.1.3. Differents amount of promoters (Cs or K)

Different cesium and potassium loadings were further investigated to find the optimum alkali loadings following the same protocol as described before. Experimental details and characterizations of the samples studied given in the SI (**Figs. S14-S17 and Tables S3-S4**). The analysis of the effect of the alkali promoter loadings further corroborates the role of the alkali addition in the inhibition of the methanation of the support, preventing the sintering of the nanoparticles and keeping the metal phase dispersion, as previously described. This structural feature is essential for the stability of the structure and the activity.

3.2. Catalytic performance

3.2.1. Effect of pyrolysis

The catalysts prepared at different pyrolysis temperatures were evaluated for ammonia synthesis reaction with a space velocity WHSV 12.000 ml g⁻¹ h⁻¹ and compared to iron Benchmark catalyst (Iron doubly promoted catalyst) Haldor-Topsoe catalyst. [17, 35, 67-69]

Fig. 4 A reveals the ammonia synthesis rates and the ammonia concentration in the reactor outlet at different pressures (0.1- 7 MPa) at 400 °C. The rates are 32117, 27783 and 18755 μmol NH₃ h⁻¹g_{cat.}⁻¹, for respectively 10-Cs-FePc₆₀₀, 10-Cs-FePc₇₀₀ and 10-Cs-FePc₈₀₀. This rate is 2 to 3-fold higher as compared to the commercial benchmark iron-based catalyst (**Fig. 4 A**).

Interestingly, the activity for the catalysts is decreasing with the increase of the pyrolysis temperature, while the iron NPs size is increasing (12, 15, and 70 nm). Nevertheless, the variation of activity with particle size is not spectacular, so we are inclined to neglect this effect of particle size on activity (**Table S5**). [70]

The stability test of the catalysts was also evaluated. There is no observed decline in activity with TOS for more than 24 h (**Fig. 4 B**). It is essential to highlight that no methane is detected during the catalytic reaction in the reactor outlet during the ammonia synthesis conditions (400 °C and up to 7 MPa). This is in full agreement with the high stability of the catalysts.

3.2.2. Effect of different alkalis

Moreover, the catalytic performance of the catalysts prepared with various alkali metals was also investigated. The NH_3 synthesis rates and the NH_3 concentration at different pressures (0.1-7 MPa) at 400 °C are shown in **Fig. 4 C and D**. The most interesting result is the significant improvement in the catalytic performance observed in the samples with alkali metals, with respect to the sample prepared without promoters. The best performances are observed for the catalyst promoted with K, and Cs, with the highest rates ~ 31.000 and $\sim 28.000 \mu\text{mol NH}_3 \cdot \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$, and ammonia concentration in the reactor outlet, 6%, and 5.4%, for 3-K-FePc₇₀₀ and 10-Cs-FePc₇₀₀ respectively (**Fig. 4 C**).

A stability test was performed at 400 °C and 7 MPa for the 3-K-FePc₇₀₀, 10-Cs-FePc₇₀₀, 1.8-Na-FePc₇₀₀ and 0.5-Li-FePc₇₀₀ catalysts. As shown in **Fig. 4 D**, there is no detectable decline in the activity for 24 h. Notably, the best catalysts (10-Cs-FePc₇₀₀ and 3-K-FePc₇₀₀) were also tested up to 72 h, without any decline activity (**Fig. S18**).

Fig. 4. The catalytic activity of the FePc derived catalysts for the ammonia synthesis. A and B different pyrolysis temperatures (600, 700, and 800 °C), **C**, and **D** with different alkali metals. **A and C:** NH_3 synthesis rate expressed in $\mu\text{mol NH}_3 \text{ h}^{-1} \text{g}_{\text{cat}}^{-1}$ at different pressures (0.1-7 MPa) at 400 °C (left) and NH_3 % in reactor outlet (right). **B and D:** Time dependence of the catalytic activities for stability test at 400 °C and 7 MPa; NH_3 synthesis rate expressed in $\mu\text{mol NH}_3 \text{ h}^{-1} \text{g}_{\text{cat}}^{-1}$ (left) and NH_3 % in reactor outlet (right). Reaction conditions: 200 mg catalyst, flow rate 40 ml min^{-1} , $\text{N}_2:\text{H}_2 = 1:3$, WHSV 12000 ml $\text{g}^{-1} \text{h}^{-1}$. No methane was detected during the catalytic reaction at 400 °C and 90.1-7MPa); the limit of detection with the Mass-vac spectrometer is less than 5 ppb.

3.2.3. Effect of promoters loading

The catalytic performance of the catalysts prepared with different Cs and K loading was also investigated (**Fig. 5** and **Fig. S20-A**). We have observed that the effect Cs loading is more pronounced as compared to K loading. As shown in **Fig. 5**, the activity is the highest for the

highest amount of Cs loading, especially when the rate is given per mol of iron, considering the Fe content. This is a spectacular effect of the alkali on the activity. This is particularly true by comparison with the sample without promotor **Fig. 5**. [71]

A stability test was also performed at 400 °C and 7 MPa for the catalysts prepared with different Cs or K loading amounts. As shown in **Figs. S19 and S20 B**, there is no detectable decline in the activity for 24 h as described previously.

Fig. 5. Catalytic performance of the FePc derived catalysts with different Cs loading for the ammonia synthesis. NH_3 synthesis rate $\mu\text{mol NH}_3 \text{ h}^{-1} \text{g}_{\text{Fe}}^{-1}$ as a function of the pressure (0.1-7 MPa) at 400 °C. Reaction conditions: 100 mg of catalyst, flow rate 40 ml min^{-1} , $\text{N}_2 : \text{H}_2 = 1:3$, with a WHSV of $24000 \text{ ml.g}^{-1}\text{h}^{-1}$.

3.2.4. Kinetic study

A kinetics analysis (order with respect to N_2 , H_2 , NH_3 partial pressures) was conducted for the most active catalysts (10-Cs-FePc₇₀₀ and 3-K-FePc₇₀₀) (**Fig. 6**). Apparent activation energies were measured at 6 MPa from the Arrhenius plots (**Fig. 6 A**). The calculated apparent activation energy was found to be 34 kJ mol^{-1} and 31 kJ mol^{-1} for the 10-Cs-FePc₇₀₀ and 3-K-FePc₇₀₀ catalysts, respectively. These values can be regarded as among the lowest values reported in the literature (**Table S6**), whereas the apparent activation energy for the benchmark catalyst is 70 kJ mol^{-1} (**Table 2**). The activation energy strongly depends on the measurement conditions

(pressure and activation conditions). Moreover, in the present work, we performed the activation energy for the FePc catalysts at 6 MPa, which is giving comparably lower activation energy as compared to our previous catalysts performed at 1 MPa.[30]

The Lower the value of activation energy itself suggests that there is a facile activation of N_2 on the catalysts surface and preferentially hydrogenated without undergoing direct dissociation on the active site of the Fe catalyst, as demonstrated by DFT calculation. The difference in the catalytic performance between 10-Cs-FePc₇₀₀ and 3-K-FePc₇₀₀ catalysts (**Figure 4 C**) could be correlated with the observed apparent activation energies. [7, 28]

Fig. 6: Kinetic parameters of 10-CsFePc₇₀₀ and 3K-FePc₇₀₀ catalysts for the ammonia synthesis reaction. **A:** Arrhenius plots at temperatures of 300–450 °C and 6 MPa. **B:** Dependence of the NH_3 -synthesis rate on the partial pressures of N_2 **B**, H_2 **C**, and NH_3 **D** at 400 °C and 1 MPa.

Table 2: Kinetic parameters of the 10-CsFePc₇₀₀ and 3-K-FePc₇₀₀ catalysts and compared to the Fe-benchmark catalyst (KM1).

Catalysts	E_a (kJ mol ⁻¹)	N ₂ order (α)	H ₂ order (β)	NH ₃ order (γ)	Ref.
^[1] 10-CsFePc ₇₀₀	34	0.53	1.3	-1.4	This work
^[1] 3-KFePc ₇₀₀	31	0.74	1.9	-1.12	This work
^[2] 10%Cs-FePc	41.9	0.68	2.10	-2.10	30
^[3] Fe-Benchmark cat.	70	0.9	2.2	-1.5	22

^[1] Arrhenius plots at temperatures of 300–450 °C and 6 MPa. ^[2] and ^[3] Arrhenius plots at temperatures of 300–450 °C and 1 MPa.

The reaction order with respect to N₂ is varying between 0.53 (Cs) and 0.74 (K) (**Fig. 6 B and Table 2**). The N₂ reaction orders for the conventional heterogeneous catalysts are usually ranging from 0.4 to 1.0. (**Table S6 in the SI**). Further, the reaction order with respect to H₂ varies between 1.3 and 1.9 (**Fig. 6C and Table 2**). The order observed in the literature for other conventional catalysts varies between 0.6 to 2.2. A value of 2 would correspond with the dissociation of H₂ on two Fe surface atoms. A value of 2.2 is reported for the commercial benchmark iron-based catalyst.

The reaction order with respect to NH₃ is -1.4 and -1.12 (**Fig.6 D and Table 2**). This observation can be interpreted in terms of the equilibrium between gaseous ammonia and adsorbed NH_x species inhibiting N₂ adsorption and activation.

The K and Cs promoted catalyst shows by far the best catalytic performance, and the increase in activity compared with the FePc₇₀₀ without promoter catalyst is supported by the substantial increase of activity with the amount of Cs and K. This improvement in activity is much more pronounced than the improvement of activity in terms of particle size. As for the objective of the present work, in order to corroborate the role of the alkali additives as structural or electronic promoters, and since it is impossible at this stage to distinguish between steric or electronic effects, a theoretical study was carried out.

Nevertheless, these alkali metals are also linked to oxygen as “K₂O” or “Cs₂O”. Therefore the active form of the catalyst is a Fe⁽⁰⁾ particle covered by various coverage of “K₂O” or “Cs₂O”. The formation of these core-shell structures appears responsible for the improvement of the activity. Due to this intimate contact between “K₂O” and “Cs₂O” with Fe, a strong metal-promoter interaction is likely occurring, thus giving rise to the enhanced catalytic activity of the promoted catalyst by the increasing of the number of active sites (**Table 3**). [70]

Table 3. Catalytic proprieties of the catalysts are prepared with various promoters.

Catalysts	Fe wt. (%)	Particle size (nm) ^[a]	Nb. of actives sites (μmol/g of sample) ^[a]	NH ₃ rate (μmol.h ⁻¹ .g ⁻¹ .cat) ^[b]
FePc ₇₀₀	80	80	208	2019
10-Cs-FePc ₇₀₀	30	15	415	27783
3-K-FePc ₇₀₀	43	11	794	30800
1.8-Na-FePc ₇₀₀	60	32	388	19760
0.5-Li-FePc ₇₀₀	51	40	263	18500

^[a]: Average Fe particle size, and number of active site were determine by TEM. ^[b]: NH₃ rate (μmol.h⁻¹.g_{cat.}⁻¹), conditions: P= 7 MPa, and T= 400 °C.

3.3. Theoretical study

3.3.1. DFT structural information

DFT calculations on the two Cs- and K-containing Fe catalysts were analyzed in order to understand the origin (geometric or electronic effect) behind the difference in their catalytic performance observed experimentally. **Fig. 7** displays the most stable structures of Fe(110)-(Cs₂O)_n and Fe(110)-(K₂O)_n catalysts (with n = 2, 3, and 4). Some of the metastable configurations, particularly for n = 4 are given in the SI (**Figs. S21-S22**). As reported in the literature, Fe(110) has been known as an active surface for ammonia synthesis but shows lower activity as compared to Fe(111) and Fe(211) surfaces. The choice of Fe(110) plane in DFT calculation is based on the XRD pattern obtained for 10-Cs-FePc₆₀₀ and 10-Cs-FePc₇₀₀ catalysts, which show a very sharp and intense peak at the 45° (2θ), corresponds to Fe(110) (Fig. S7), which

is the most abundant and stable surface. Therefore, we chose Fe(110) plane to perform the DFT calculations, which might help to inspire the real catalyst structure.

In both cases, the structures were highly unstable when all the O species are located above the alkali species without the formation of any Fe-O bond. However, their stability was getting systematically enhanced when more and more O species are intercalated in between alkali layers and Fe surface (**Figs. S21-S22**).

The structures were finally strongly stabilized when all the O species are intercalated in between the alkali layers and Fe surface with the maximal number of Fe-O bonds (**Figs. S21-S22**). In the lowest-energy structures, the Cs, K, and O species are homogeneously distributed over the Fe(110) surface and preferentially adopt a double-layer structure where the first sublayer on top of the iron surface is made by O species and the second layer above the first one is made by Cs or K species, as shown in **Fig. 7**.

The most stable structures reveal well-oriented and dispersed " Cs_2O " and " K_2O " species, in which each O species is sitting on a triangle of Fe with O-Fe bond length of 1.9 Å and the two neighboring alkali elements are sitting on squares of Fe with Cs-Fe non-bonding distances ranging from 3.3 to 3.8 Å, Cs-O bond length of 2.9 Å, K-Fe non-bonding distances ranging from 3.1 to 3.4 Å, and K-O bond length of 2.8 Å. The " Cs_2O " species are separated between each other by nearest Cs-Cs distances ranging from 4.7 to 7.9 Å with decreasing Cs loading from $n = 4$ to $n = 2$. The " K_2O " species are separated between each other by larger nearest K-K distances ranging from 4.6 to 7.9 Å with decreasing K loading from $n = 4$ to $n = 2$. These results lead to almost complete coverage of Fe surface, in good agreement with the obtained HAADF-STEM images of 10-Cs-FePc and 3-K-FePc catalysts (**Fig. 2**).

Our predicted structures are in pretty good agreement with the previous work published by Arabczyk and co-workers. [61] Interestingly, as Cs size is much larger than K, almost all of Cs species are deposited on squares of Fe while some of K species are displaced from Fe squares towards other neighbor K species in order to bind strongly with O and maintain the same K-O bond length of 2.7 Å.

This leads to a more significant number of exposed Fe atoms in the case of K than Cs, as highlighted in **Fig. 7**. As a consequence, the number of active sites is expected to be larger in the case of K than Cs, and therefore, this geometrical discrepancy is expected to leave an impact on the catalytic performance results, as observed in **Fig. 4**, described before.

The thermodynamic stability was also studied by DFT calculations to evaluate the possible formation of Fe(110)-Cs_{2n} and Fe(110)-K_{2n} catalysts by treating Fe(110)-(Cs₂O)_n and Fe(110)-(K₂O)_n catalysts under hydrogen following the experimental conditions and the possible release of water from the reaction. The thermodynamic diagram is shown in **Fig. 8**. As can be clearly seen, Fe(110)-(Cs₂O)_n and Fe(110)-(K₂O)_n catalysts are thermodynamically much more stable than Fe(110)-Cs_{2n} and Fe(110)-K_{2n} catalysts throughout this hydrogen chemical potential.

This result confirms the necessary presence of O species in line with the experimental observations. In order to get relevant information about any possible direct electron transfer between Cs or K and Fe support, the analysis was performed on the most stable structures of Fe(110)-(Cs₂O)_n and Fe(110)-(K₂O)_n catalysts. In both cases, Bader charge analysis revealed slightly positive charges of Fe linked to O (with a loss of 0.2 fractions of the electron; Fe^(+0.2)). While those directly coordinated with Cs and K, or even the exposed surface Fe revealed slightly negative charges (with a gain of 0.1 to 0.16 fraction of electron; Fe^(-0.13)).

By comparing the DFT-based predicted atomic and electronic structures of Fe(110)-(Cs₂O)_n and Fe(110)-(K₂O)_n catalysts, we could see a similarity in the charge distribution of surface Fe species, while the main discrepancy was related to the geometrical repartition of alkali species. This fundamental aspect might explain the difference in the catalytic results. This corroborates that geometrical effect becomes more important than the electronic impact in the role of alkali metal additives.

Fig. 7. Top view depictions (8 x 8) of the DFT-based most stable structures of $\text{Fe(110)-Cs}_2\text{O}_n$ (on the left) and $\text{Fe(110)-(K}_2\text{O)}_n$ (on the right) catalysts with $n = 2, 3$, and 4. Color legend: Fe in green, Cs in dark purple, K in light purple, O in red, and exposed Fe in pink. The number of surface atoms is given above each structure. The number of exposed Fe atoms is given below each structure.

Fig. 8. DFT-based computed formation energy of $\text{Fe}(110)\text{-(Cs}_2\text{O)}_n$ and $\text{Fe}(110)\text{-(K}_2\text{O)}_n$ catalysts as a function of hydrogen chemical potential at 400 °C with released water at atmospheric pressure. The dashed red line with zero formation energy represents $\text{Fe}(110)\text{-(Cs}_2\text{O)}_n$ and $\text{Fe}(110)\text{-(K}_2\text{O)}_n$ catalysts.

3.3.2. DFT mechanistic information

Finally, DFT calculations were also carried out to illustrate the mechanism of N_2 activation and reduction to ammonia. The modeling of the reaction pathway was conducted, especially on a medium loading of K as a typical example. **Fig. 9** illustrates the change in the free energy profile with pressure, at a temperature of 400 °C. Since the experiments were performed in excess of H_2 and high pressure of 7 MPa, we first adsorbed three dihydrogen on $\text{K}_2\text{O/Fe (110)}$ consecutively. The three H_2 are adsorbed dissociatively (binding energy ranging approximately between -20 to -30 kcal.mol^{-1}) on the Fe surface near the K_2O clusters. Dinitrogen is adsorbed near this dissociated H_2 with a binding energy of $\sim -15 \text{ kcal.mol}^{-1}$ by an end-on-mode (non-dissociative) (**Fig. 9**). The triple $\text{N}\equiv\text{N}$ bond is subsequently cleaved with gradual hydrogenation of the specific N atom not bound to Fe, leading stepwise to the release of the first NH_3 molecule. This type of NRR (nitrogen reduction reaction) is classified by previous studies as a distal associative pathway.[72, 73] The second NH_3 is also thermodynamically favorable as the first NH_3 is released from the surface. As seen in the free energy profile of **Fig. 9**, the intermediates become thermodynamically more feasible with increasing pressure. At atmospheric pressure and 400 °C, N_2 adsorption is thermodynamically unfavorable (by $\sim 10 \text{ kcal.mol}^{-1}$) in the presence of excess H atoms on the Fe surface. As the pressure increases to 1 MPa, the reaction profile becomes downhill, and the N_2 is adsorbed at $\sim 7 \text{ kcal.mol}^{-1}$, the binding energy gradually increases with increasing pressure. Therefore, the thermodynamic stability of the reaction intermediates for NRR increases with increasing pressure. This indicates better feasibility of the ammonia production at higher pressures, which is in good agreement with the experimental data described previously (**Fig. 4**).

As a conclusion of the DFT studies on the localization of promoters and the resulting mechanism, we can say that, in agreement with experiment results, the promoters are localized on the $\text{Fe}^{(0)}$

as " K_2O " or " Cs_2O ". This coordination leaves some free space for $\text{Fe}^{(0)}$ and molecular N_2 coordination. This coordination is "end on" on a unique Fe atom. Then, there is a progressive stepwise addition of hydrogen on the distal N and the closer N leading to ammonia.

Fig. 9. Gibbs free energy (ΔG) profile close to the experimental reaction temperature of 400 °C of N_2 hydrogenation to NH_3 on $\text{K}_2\text{O}/\text{Fe}$ (110). The insets are zoomed c-view of the surface where the hydrogen attack the N_2 to show the geometries of the reaction intermediates. The corresponding DFT-based geometries of the intermediate structures of NRR to the ChemDraw drawings are given in the SI (**Fig. S23**).

4. Conclusion

In summary, we have successfully prepared Fe NPs supported on carbon by pyrolysis of FePc under N_2 followed by treatment under H_2 . These NPs were found to be very active and stable

catalysts for ammonia synthesis, as compared to the commercial iron-based catalyst from Haldor-Topsoe, widely used for the ammonia synthesis process.

Extensive characterization was applied at various stages of the preparation. Nano-sized core-shell structures were formed during H_2 pretreatment, with Fe NPs located in the core and oxygen-alkali metals located on the shell. The alkali metals and their loading played critical roles in the particle size distribution. They also partially inhibited the methanation process of carbon, which occurs during the H_2 pretreatment. Increasing the pyrolysis temperature increased the iron particle size and encapsulation of iron into the carbon support was observed at ca. 800 °C.

The activities for FePc catalysts promoted with various promoters followed the order: $K > Cs > Na \sim Li$. The optimal catalytic performance was obtained with a catalyst prepared by pyrolysis at 600 °C promoted with 10% wt. Cs or at 700 °C promoted by 3% wt. of K, reaching more than 6% of NH_3 at 400 °C and 7 MPa at a WHSV of 12000 $ml.g^{-1}.h^{-1}$, with no observable deactivation over 72 h.

The apparent activation energy for ammonia synthesis was found to be 31 $kJ.mol^{-1}$ and 34 $kJ.mol^{-1}$ for 3-K-FePc₇₀₀ and 10-Cs-FePc₇₀₀ catalysts, respectively, suggesting the facile activation of N_2 on the catalysts surface. Further, kinetic studies reveal the reaction order with respect to N_2 is close to unity (0.7). The reaction order with respect to H_2 is close to 1.5, suggesting the dissociation of H_2 on two Fe surface atoms. The negative order (-1.3) with respect to NH_3 suggesting that ammonia is equilibrium with the NH_x species on the catalysis surface. The main discrepancy was related to the geometrical repartition of alkali species, leading to a larger number of exposed iron, active sites, in the case of K than Cs.

The predicted thermodynamic results showed that the alkali present under the form of " M_2O " (M= Cs and K) cannot be reduced even at high temperature and hydrogen pressure, confirming the necessary presence of O species in line with the experimental observations. The metal oxide leaves at medium coverage of the surface some exposed iron for N_2 non-dissociative chemisorption (end-on type).

Regarding the mechanism of ammonia synthesis at a molecular level, a DFT-based mechanistic study for N_2 activation and reduction was conducted mainly for Fe(110)-K₂O catalyst. The free energy profile demonstrated that the thermodynamic stability of the reaction intermediates for Nitrogen Reduction Reaction (NRR) increased with increasing pressure, indicating better feasibility of the reaction at higher pressures, which is in good agreement with the experiment data.

This study, based on an in-depth analysis of the structure-activity relationship, allowed us to bring a precise picture of the role of the alkali metals in the ammonia synthesis process. Furthermore, DFT calculations were also applied to probe the feasibility of associative mechanism with the stepwise addition of hydrogen, as we have previously demonstrated on a single Ta atom on silica.[18] This observation still opens the question of the role of dissociated forms of nitrogen (NH_x), which are certainly observed under certain conditions. They have been claimed as intermediates in the mechanism of ammonia synthesis, but the main conclusion of this DFT mechanistic approach seems to indicate that they are not involved in the mechanism of ammonia synthesis.

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Conflict of interest

The authors declare no conflict of interests.