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A review of multiscale modelling approaches for understanding catalytic ammonia synthesis and decomposition

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ABSTRACT

Ammonia plays a crucial role in our lives as it is widely used, for example, in the synthesis of fertilizers, the production of carbon-free hydrogen for fuel cells, or electricity generation. However, the conventional Haber-Bosch process for ammonia synthesis has several drawbacks, such as requiring high temperatures and pressures, consuming 1–2% of the world's energy supply. While significant progress has been made in performing the reaction under milder conditions, the subject has experienced a second renaissance with the advent of multiscale modeling and improvements in computational capabilities.

Multiscale modeling at various levels, including density functional theory (DFT), transition state theory (TST), kinetic Monte Carlo method (KMC), microkinetic modeling, molecular dynamics (MD), and computational fluid dynamics (CFD), allows us to describe the reaction system at all levels simultaneously. In this review, we focus on the treatment of ammonia synthesis, decomposition, or oxidation using multiscale models, ranging from the study of quantum-level interactions to the optimization of reactor design.

Recently, significant progress has been made in modeling. Current modeling tools, while well developed, still have weaknesses in their linkage. DFT /TST is often coupled with KMC and MD or microkinetic data are fed into CFD while a comprehensive model is lacking. The potential for further progress through the use of multiscale models is enormous, which could lead to more efficient catalyst and process design.

1. Introduction

Despite being over 100 years old, the Haber–Bosch process remains the most important industrial route for ammonia synthesis. Ammonia is produced from N_2 and H_2 at high temperatures (500 °C) and pressures (up to 200 bar), which causes high energy expenditures. [12] Hence, the process has been thoroughly investigated over the years to reduce the energy required [3] by making the reaction feasible at milder conditions. This is done both by optimizing the catalysts and improving the process itself. [245] In addition to the conventional thermocatalytic approach, biological processes such as biological nitrogen fixation with bacterial nitrogenase enzymes has also attracted great interest since it could operate under ambient temperature and pressure. [67].

Historically, Fritz Haber developed the ammonia synthesis process from H_2 and N_2 at an increased temperature (500 °C) and pressure (100 atm) in 1909. Carl Bosch industrialized the process and put Haber's lab scale machine into an 8 m tall reactor for upscaling to 115 g/h at that time. [8910] Fitz Haber, Carl Bosch, Alwin Mittasch and Gerhard Ertl are credited with the most visible contributions to creating and developing the synthetic ammonia synthesis process. Ever since, synthetic ammonia has had a major impact on the world, specifically for food production by allowing to mass-produce fertilizers. The invention of the Haber-Bosch process is often heralded as one of the most important achievements of the modern society as it has made the population increase possible. [28910].

While the original Haber-Bosch (HB) process has been a focus of research throughout its 100-year history, improvements were made mainly on the production capabilities, which have ultimately increased the global production from around 1800 tonnes yearly to more than 183 million tons per year. [211] Much less has been achieved in terms of

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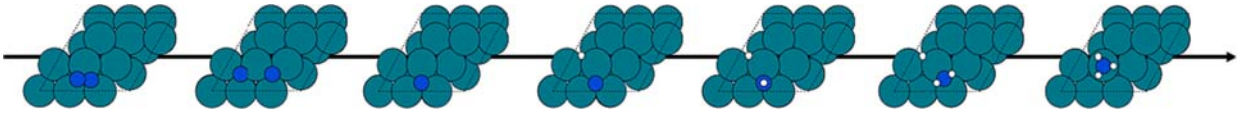

Fig. 1. Surface reaction steps during ammonia synthesis over a Ru (0001) catalyst. Own work, mechanism . adopted from [26]

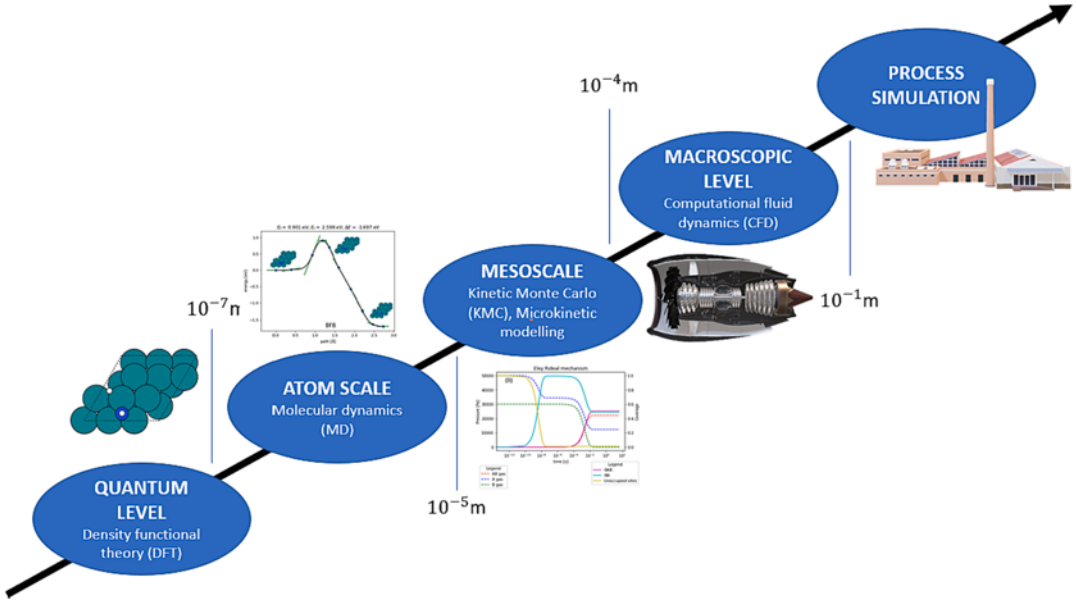

Fig. 2. Multiscale modelling steps from quantum level to process simulation level.

energy consumption, although some progress was also made in finding milder process conditions as the initial process required a pressure of around 100 MPa. [211] Currently, the process is run at 10–20 MPa. However, the HB process still contributes 1–2 % of the global energy consumption. Furthermore, a major problem are the CO_2 emissions, which stem from the energy expenditure and the production of H_2 as feedstock. It is estimated [2] that 400 Mt of CO_2 are released annually due to ammonia production, which represent 1.6 % of the global CO_2 emissions. [29].

Most improvements of the HB process focused on the catalysts. In 2007, Gerhard Ertl won the Nobel Prize for Chemistry for his research on surface chemistry of the iron catalyst.[12] Iron catalysts remain the most studied catalysts for HB and due to their low price industrially most used. A second generation of catalysts use Ru, which exhibits better performance at milder conditions but are plagued by relatively high cost. Recently, ruthenium, nickel, cobalt and metal nitrides have been studied for promoting the iron catalyst in industrial ammonia synthesis processes. Moreover, catalysts using electrides, hydrides, amides, nitrides, oxynitride hydride and oxide support materials have been proposed as possible alternatives to Fe and Ru catalysts, as well as Co and Ni catalysts. [913] In addition to searching for the catalyst effective at milder conditions, alleviating oxygen poisoning at low temperatures is another aspect. [14].

In addition, significant progress has been made in the realm of ammonia synthesis electrification, which has the potential to drastically lower CO_2 emissions compared to the conventional HB process provided green electricity is used. The design of catalysts and cells is a crucial aspect of electrochemical nitrogen reduction reactions (eNRR). There are several promising examples, such as the use of dual-atom catalysts with transition metals embedded in graphene with four neighbouring nitrogen atoms (T M_4N_4@graphene) [15], Au carbon nanotube catalysts for eNRR under ambient conditions [161718], Fe-CuS/C for ammonia synthesis at low temperatures and atmospheric pressure [19], and Ru-catalysed eNRR in a gas diffusion flow cell [20]. These examples show how eNRR could be utilized in the future, provided the efficiency problem is solved and/or abundant cheap energy is available. [18].

While the HB process has been extensively modelled at various scales, recent advances in the available computational power and method development have brought idea of multiscale modelling to fruition. For better understanding, researchers use multiscale modeling techniques to observe the reaction from atomistic scale to reactor level. Ultimately, multiscale models can lead to digital twins, which are full in silico description of every unit operation in a plant. [21] For instance, it should be possible to model an ideal (or at least improved) catalyst for the reaction, determine the optimum reaction conditions, reactor set-up and calculate yields, conversions and selectivity for these parameters. °.

Ammonia is also being investigated for use as a long-term chemical storage of hydrogen. When employed as a hydrogen carrier that is devoid of carbon, an efficient decomposition of ammonia is required for its utilization. While ammonia decomposition has not reached the necessary maturity for a widespread industrial adoption as an energy vector, it is currently applied industrially mainly for annealing metals and galvanizing. The ammonia crackers use external energy sources, nickel supported on aluminium oxide as catalyst, and operate at a temperature of about 850–950 °C. [22]. Consequently, several studies – mainly experimental – have focused on using Ni catalysts. [22232425].

In this work, we review the multiscale modelling approaches to ammonia synthesis and decomposition over various catalysts. We show the recent progress in terms of modelling different scales and in particular their coupling. Historically, various catalysts have been used and modelled for ammonia synthesis. We follow the historical evolution of different catalysts. First, iron catalysts as the first-generation catalytic materials are described since they are still amply used due to cost considerations. Later on, modelling efforts on Ru catalysts are discussed as promising second-generation catalysts, which must be optimised in terms of catalyst loading due to prohibitive price of the metal. In the end,

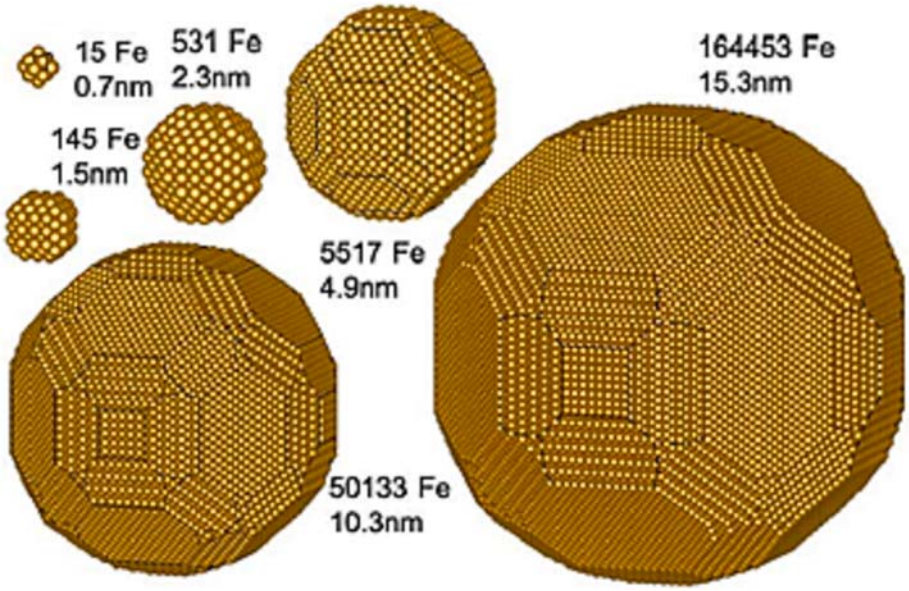

Fig. 3. Fe particles (0.7 nm – 15 nm) modelled by Zhang et al. [53].

novel catalysts, such as other transition metals and alloys are described. In all instances, different levels of modelling are discussed and how they can be linked. Mechanism of ammonia synthesis over Ru (0001) is presented in Fig. 1 (the mechanism adopted from Zinalipour-Yazdi et al. [26]).

2. What is multiscale modelling?

Multiscale modeling is a computational approach of studying processes on different scales as shown on Fig. 2. While according to the technical definition at least two scales must be coupled, it can be used from the atomistic level, to the kinetic or mesoscale scale and finally the reactor level. [2728] Multiscale modelling involves solving different mathematical models in various fields, such as material science, chemistry, fluid dynamics, biology, etc. [29] It enables us to optimise processes, investigate and design new materials and catalysts and propose optimum reaction conditions and vessels. Although the models included are usually complex and computationally expensive, it is becoming increasingly used in catalyst discovery and tailoring, materials science, reactor design and performance (selectivity, yield, conversion) predictions. [2830–33].

Atomistic scale. When used for describing chemical processes, multiscale modeling often consists of three scales. At the lowest scale, the quantum or electronic level, the atomic structure and the interplay of electrons is studied. In modelling heterogeneous catalytic reactions, one is interested in the gaseous reactions (if applicable), adsorbate–surface interactions, surface reactions and adsorbate–adsorbate interaction. The most commonly used method to obtain the electronic structure is the density functional theory (DFT), which has a favourable cost/performance ratio. [27] DFT is also used for studying the molecular properties, geometries and structures, bioinorganic systems, chemical reactions etc. [343536].

To understand the reaction mechanism, DFT results are then used in the transition state theory (TST), which provides reaction rates at different conditions, while molecular dynamics yields dynamic properties, such as diffusion coefficients. [27283738].

Mesoscale. After the atomistic level, the meso scale represents the next step in multiscale modeling, focusing on the kinetics of a specific system. Granular surface kinetics can be observed using kinetic Monte Carlo (KMC), which is used to follow adsorption, surface diffusion, adsorbate reactions, defects evolution etc. While KMC is used for complex heterogeneous systems, where particle–particle interactions are strong, however, microkinetic modeling in terms of solving differential equations is a more common and computationally cheaper way, useful when the mean-field approach is warranted. [272837] On the other hand, KMC is needed to study surface diffusion, creation, propagation and modification of defects etc. [39].

Recently, the use of machine learning has supplemented other approaches as it can potentially bring about substantial savings of the computational cost. Here, the training part is most time consuming but the speed-up in its use is then exponential. This is particularly useful for AIMD simulations, where the DFT calculations are the bottleneck. Historically, force-fields – empirical or analytical – were often used instead to speed up MD calculations. Recently, new machine-learning generations of force-fields are increasingly being used. Zhang et al. have elucidated the relationship between molecular simulations and the potential enhancements that artificial intelligence can bring to the field [40] and in general [41]. Machine learning has proven to be instrumental in improving the accuracy of MD simulations, expediting the development of superior models, and extending the reach of high-quality electronic structure theory [42].

At the mesoscale, it is possible to include coverage phenomena. These are often crucial when reconciling experimental data with simulations, especially when experimental conditions are harsh, such as during ammonia synthesis. Pair-wise interactions with the atomistic granularity can be included in kinetic Monte Carlo simulations, while mean-field microkinetic modelling can at least average them. Moreover, coverage phenomena are paramount when describing catalyst poisoning or deactivation, which is one of the major problems in heterogeneous catalysis. For instance, Movick et al. investigated ammonia synthesis reaction over the Ru catalyst at low temperatures and found out that at higher temperatures (350 – 400 °C), the degree of poisoning is reduced. On the contrary, in the low temperature regime (225 – 250 °C), coverages with hydrogen as well as intermediates (NH_x) are substantial. [43] Chen et al. studied the activity trends over a Fe catalyst account for coverage effects using DFT and microkinetic modelling, obtaining a good agreement with experimental results. [44] Although some studies have included surface coverage dependency, for instance over Ru on $(BaO)_x(CaO)_y(Al_2O_3)_z$ [45], barium promoted Ru catalyst [46], Ru/CeLaTi O_x [47], this is not yet common-place.

Reactor scale. Lastly, reactor-scale or even industrial plants design modelling can be performed. To describe the macroscopic phenomena in

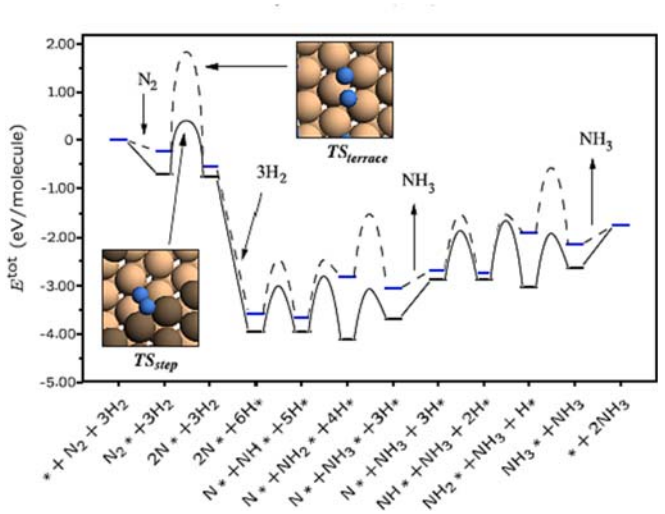

Fig. 4. Ammonia synthesis mechanism; energy diagram by Hellman et al. [59].

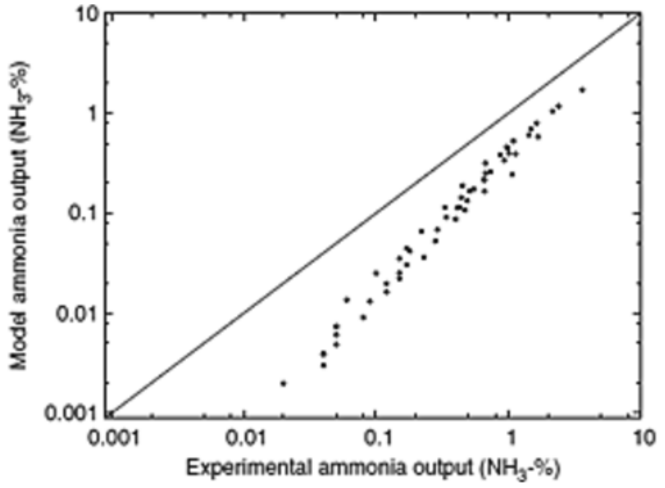

Fig. 5. Comparison between theoretical and measured productivity by Hellman et al. [59].

a reactor, computational fluid dynamics (CFD) can be employed. Particle-resolved CFD models can also describe the reaction at the pore diffusion scale, when relevant, by coupling reaction–diffusion. [48] The data from the lower scales can be combined in a simulation of a realistic system, i.e. a reactor, at the desired conditions. Relevant parameters, such as concentrations or pressure, can be determined throughout the reactor in order to theoretically optimise the design of the entire system. CFD calculations can elucidate the effect of the reactor design and reaction conditions on the performance. [49] Nowadays, CFD has become the computational workhorse in reactor design, showing great performance for single-phase reactors and great potential for describing multiphase reactors. [50] At the plant level, process modelling with ASPEN is possible. Multiscale modelling is of particular importance because simulations at disconnected levels can give different predictions than an all-encompassing model.

We wish to emphasize that while the multiscale modelling approach is applicable to different reactions, it can easily be adapted to study the same reaction in the other direction if desirable. Ammonia decomposition is such an example as it *can* also proceed on similar catalysts (albeit at different conditions) as ammonia synthesis or not. For instance, Boisen et al. [51] showed in with their DFT calculations and microkinetic modelling, yielding volcano plots, the optimal catalyst for ammonia synthesis is different than for ammonia decomposition reaction. However, the authors suggest that understanding ammonia synthesis is relevant for ammonia decomposition reaction, as well.

3. Iron-based catalysts

The Haber Bosch process is still predominantly based on Fe catalysts due to their lower price and lower toxicity in comparison to more efficient Ru catalysts. The performance of Fe catalysts has remained an important avenue of research since the invention of the process.

DFT + KMC modelling. Qian et al. [52] investigated ammonia synthesis over Fe(1 1 1) using DFT and KMC. The authors postulated a detailed reaction network, including the Langmuir Hinshelwood and Eley Rideal mechanism. Coupling DFT and KMC in a multiscale model, a good agreement of the calculated TOF (17.7 s^{-1} at 673 K and 20 atm on a 2x2 site) with the experimental values (10 s^{-1}) was observed.

DFT + Wulff construction. Addressing the implications of particles size on catalyst design, Zhang et al. [53] studied different Fe nanoparticles (Fig. 3), as predicted with the Wulff construction. They modelled the particle of different sizes using DFT and observed the effect of intrinsic activity and density of active sites on the overall reaction activity. Fe (1 1 1)- and Fe (3 1 1)-containing particles have highly active C7 sites but are limited by low surface area. Surfaces, such as Fe (1 1 0) with high surface area are on the other hand limited by low intrinsic activity. Fe (2 1 1), Fe (3 1 0) and Fe (3 1 0) exhibited the highest reactivity with Fe particles greater than 6 nm due to C7 and B5 sites. Interestingly, the authors reported a decrease in *reactivity for smaller particles because of fewer C7 and B5 sites.*

An *et al.* also demonstrated the effect of Fe nanoparticles on ammonia synthesis when they investigated the effect of nanoparticle shapes on ammonia synthesis. After testing 34 different dopants, the authors observed that Si or Ni increase the rate of the reaction the most. [54] A similar hierarchical high-throughput catalyst screening (HHTCS) approach was done by Fuller et al. and identified Co, Ni and Si as high performance dopands. [55].

DFT + microkinetic simulations. The detailed mechanism of ammonia synthesis over $Fe_3/\theta-Al_2O_3(0\,1\,0)$ was investigated by Liu et al. [56], determining the most favourable reaction path on a proposed active centre of the Fe_3 cluster, using DFT and microkinetic simulations. The associative mechanism was found to predominate with the N-NH species being the key intermediate. Furthermore, they concluded that associative mechanism at single cluster is faster than dissociative mechanism. The calculated TOF values for $Fe_3/\theta-Al_2O_3(010)$ catalyst were comparable to TOFs over Ru B5 site, purporting the Fe_3 centers as promising candidates for highly selective ammonia synthesis.

Catalyst screening. An et al. [57] studied a Si-doped Fe catalyst, which was identified in a hierarchical high-throughput catalyst screening mechanism, which was used to investigate only the reaction steps that might be rate determining. After calculating free energy barriers researchers estimated how dopands modify their rate determining steps barriers. Using a kinetic Monte Carlo model to compare Fe and Si-doped Fe, the latter achieved similar TOFs under milder conditions.

4. Second-generation Ru catalysts

4.1. Ammonia synthesis

Second-generation catalysts for ammonia production are based on Ru. Since they exhibit superior performance in terms of selectivity, yields and the required conditions, Ru has remained one of the most investigated catalysts. In addition to tailoring the catalyst to perform under milder conditions, formulations with low Ru mass fraction are much sought after for economic reasons. In this section, we present multiscale modeling approaches for Ru-based catalysts for ammonia synthesis and decomposition.

DFT. Hellman et al. [58] studied ammonia production over a stepped

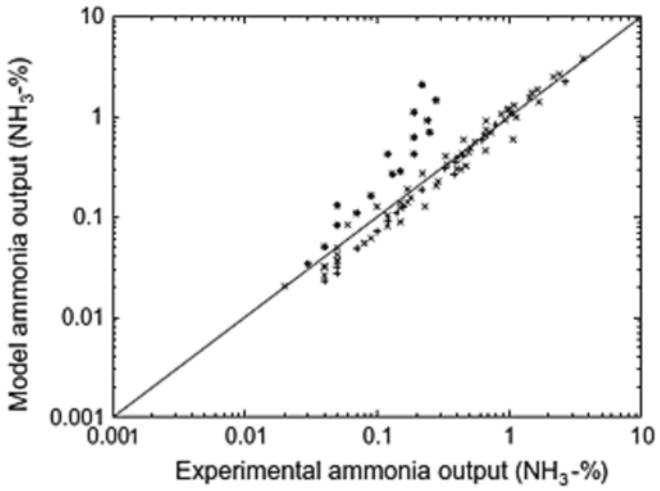

Fig. 6. Theoretical ammonia productivity in comparison to measured productivity by Hellman et al. [69].

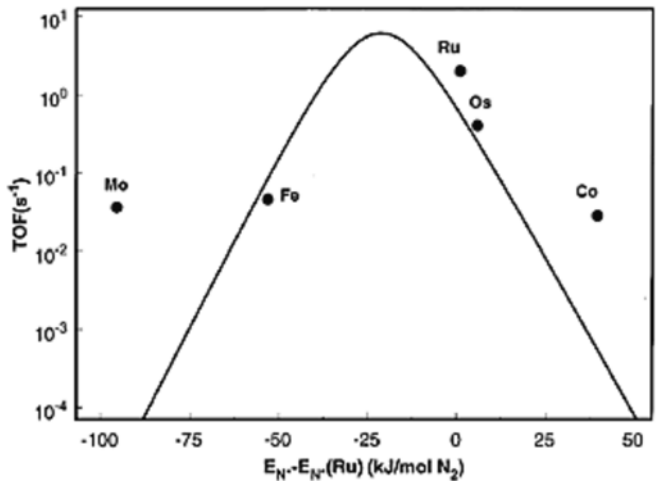

Fig. 7. Volcano curve for ammonia synthesis reaction at 0.8 bar, 588 K, H_2 : N_2 = 3 by Jacobsen et al. [78].

1. $N_2(g) + 2* \leftrightharpoons 2N^*$
2. $H_2(g) + 2* \leftrightharpoons 2H^*$
3. $N^* + H^* \leftrightharpoons NH^* + {}^*$
4. $NH^* + H^* \leftrightharpoons NH_2^* + {}^*$
5. $NH_2^* + H^* \leftrightharpoons NH_3^* + {}^*$
6. $NH_3^* \leftrightharpoons NH_3 + {}^*$

Scheme 1. Reaction mechanism for ammonia synthesis reacton over dissociative mechanism.

Ru (0001) surface on the atomistic scale, using DFT with the transition state theory (TST). They investigated reaction mechanism pathway and constructed a kinetic model for ammonia productivity prediction for industrial relevant catalyst. Researchers found out that by applying various levels of theoretical research such as DFT, TST, kinetic

1. $N_2 + \frac{1}{2}H_2 + 3* \leftrightharpoons N_2H^{**} + {}^* + *$
2. $N_2H^{**} + H^* \leftrightharpoons N_2H_2^* + 2*$
3. $N_2H^{**} + H^* \leftrightharpoons NH^* + N^* + H^*$
4. $NH^* + H^* \leftrightharpoons NH_2^* + {}^*$
5. $NH_2^* + H^* \leftrightharpoons NH_3^* + {}^*$
6. $NH_3^* \leftrightharpoons NH_3 + {}^*$

Scheme 2. Reaction mechanism for ammonia synthesis reaction over associative mechanism.

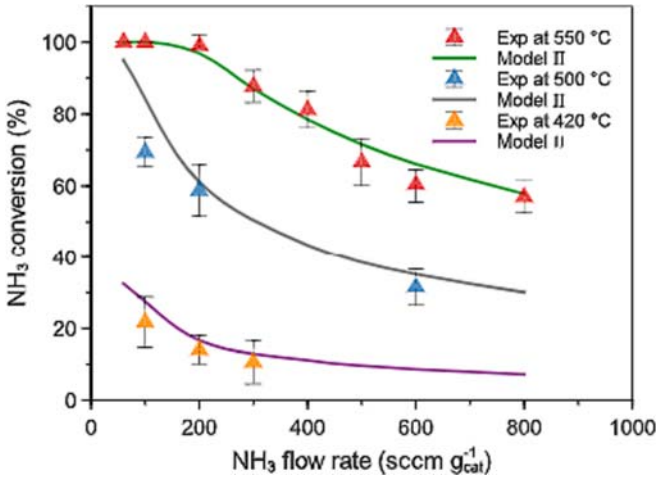

Fig. 8. Experimental and modelled ammonia conversions for different ammonia flow rates and reaction temperatures by Maleki et al. [96].

modelling they are able to predict overall rates of ammonia production. Their kinetic model was able to predict the ammonia productivity within a factor of 3–20 for the industrial relevant catalyst. They also point out the importance of theoretical modelling for process investigation and claimed theoretical modelling will become one of the most important tools in investigation of next generation of catalysts.

DFT + KMC modelling. Using their first-principles model, Hellman et al. [59] compared experimental data for ammonia synthesis on an unpromoted Ru catalyst with theoretical predictions for a multiscale model. This consisted of a DFT level over Ru flat surface as well as the stepped surface (with B_5 sites) for energetic calculations of the reaction mechanism (Fig. 4), kinetic Monte Carlo simulations to simulate the catalyst coverages and a kinetic model to model the effect of reaction parameters and conditions, such as inlet flow and partial pressures. The theoretical values agreed well with the experiments (Fig. 5).

Logadottir et al. [60], studied the reaction on a Ru(0001) surface. Using DFT, the dissociative mechanism was proposed and the reaction was found to occur on step sites as opposed to terraces where nitrogen dissociation was the rate-determining step.

DFT + MD. Kim et al. [61] studied Ru nanoparticles using first-principles-based MD simulations with ReaxFF, determining the activity, selectivity and durability of the catalyst. Investigating the size effect on the energy barrier for nitrogen dissociation and catalytic performance at 1500 K. The catalyst exhibited the greatest activity with 4 nm nanoparticles (number of dissociated N atoms per surface area is $5.09*10^{18}m^{-2}$) due to the highest surface area, but the best selectivity

Table 1
Table where researcher that used multiscale modeling for ammonia synthesis, decomposition and oxidation reaction. Reference of specific research is written as well as reaction type, catalyst used, multiscale methods, that were used in specific research as well as reaction/modeling conditions and brief description of each research.

	Source	Ammonia synthesis(S), decomposition (D), oxidation (O)	Catalyst used	Multiscale methods	Reaction conditions	Remarks
1	[67]	S&D	Ru/Al2O3	DFT, CFD	T = 600–1000 °C	Microkinetic analysis implemented in CFD calculations.
2	[72]	D	Ru/γ-Al2O3	DFT, Monte Carlo	/	High throughput multiscale was used.
3	[73]	D	Ru catalyst	CFD	T = 300 K (inlet) P = 1 atm	2D CFD studies of multifunctional microscale reactors.
4	[74]	D	Ru/Al2O3	DFT, CFD	T = 300 °C (initial)	CFD modeling for H2 production.
5	[58]	S	Ru catalyst	DFT, TST	T = 200–750 K (large interval of temperatures was investigated)	Ammonia gas phase chemistry with multiscale modeling.
6	[62]	S	Ru/Ca2NH	DFT, MD	T = 200–360 °C	Focus is on Ru/Ca2NH as transition metal-loaded electride family.
7	[83]	D	Single metal catalyst: Co, Pt, Pd, Ni, Ru, Rh, Ir, Re, Mo Catalyst II: Ni-Pt-Pt (1 1 1)	DFT, Microkinetic modeling	Various temperatures: 850 K, 325 K (Ni-Pt-Pt)	Predicting suitable monolayer bimetallic system, furthermore tested.
8	[61]	S	Ru nanoparticle catalyst	DFT, MD	T = 700–1500 K P = 300–1000 atm	Investigation of Ru nanoparticle catalyst.
9	[80]	S	15 transition metals 3 top catalysts: Ru, Co, Ni	DFT, Microkinetic modeling	T = 525 K, 600 K P = 10 bar	Theoretical research of ammonia synthesis catalyst activity acceleration using special confined dual site.
10	[70]	D	Ru catalyst	DFT, TST, Monte Carlo, Microkinetic modeling	T = 500–1000 K P = 0.1–10 atm	Multiscale research and experiments design of ammonia decomposition over Ru catalyst.
11	[69]	S&D	Ru catalyst	DFT, Monte Carlo	T = 593–713 K P = 50–100 bar different H2:N2 ratios	Modeling ammonia synthesis and decomposition processes from first-principles, varying reactants ratios as well as temperature and pressure.
12	[65]	D	Ru @ CNT	DFT	/	Investigation of rate limiting step, the effect of Ru size, various Ru sites are investigated.
13	[79]	S	Screening TM/g-C_3N_4 Pt-g-C_3N_4	DFT, MD	T = 300–350 K	Screening of possible transition state catalysts, defining best TM (Pt), first-principles study.
14	[98]	S	Ru/Mg Al_2O_4	DFT, KMC, TST	T = 320–440 °C	Kinetic description considering complex interactions under industrial conditions over packed bed of nanoparticle catalyst with high surface area.
15	[84]	D	High entropy alloy catalysts CoMoFeNiCu nanoparticles	DFT, KMC	T = 250–600 °C (catalytic activity measurements); MC simulations: 573 K, 750 K and 1000 K	Authors investigated high entropy alloy catalysts for ammonia decomposition reaction.
16	[87]	D	Ni on Pt	DFT, KMC	T = 300–600 K	Multiscale calculation, varying the size and shape of Ni clusters on Pt.
17	[59]	S	Ru catalyst	DFT, KMC	T = 320–440 °C P = 50 bar	First-principles calculations, macro properties calculations, various reaction conditions.
18	[93]	S	Ni/BaH_2	DFT, MD	/	First-principles simulation of Ni/Ba H_2 transformation during ammonia synthesis from N_2H_2
19	[92]	D	Ni (1 1 0)	DFT, kinetic analysis	T = 350 K P = 1 atm	First-principles calculations of ammonia decomposition reaction over Ni(1 1 0)
20	[78]	S	Volcano curve calculation (Ru, Fe, Mo, Os, Co)	DFT, Microkinetic modeling	T = 300 K − 550 K	Volcano curve for catalyst and optimal process conditions for ammonia synthesis was calculated
21	[57]	S	Si doped Fe catalyst	DFT, MC	T = 773 K, P = 20 atm T = 673 K, P = 60 atm	Investigation of ammonia synthesis reaction over Si doped Fe catalyst under milder conditions
22	[88]	D	NiPt	DFT, KMC	/	Catalyst microstructure optimisation
23	[82]	S	Plasma	DFT, Microkinetic modeling	/	Review article about plasma catalysis and plasma driven ammonia synthesis
24	[86]	D	Ir(1 0 0)	DFT, Microkinetic analysis	/	Ammonia decomposition mechanism was investigated and computational methods were used to investigate Ir(1 0 0) catalyst
25	[71]	D	Ru/γ-Al_2O_3	DFT, Microkinetic modeling	T = 360–460 °C	Models as well as experimental design is presented in ammonia decomposition reaction investigation over Ru/γ-Al2O3

(*continued on next page*)

Table 1 (*continued*)

	Source	Ammonia synthesis(S), decomposition (D), oxidation (O)	Catalyst used	Multiscale methods	Reaction conditions	Remarks
26	[89]	D	Ni/Pt	DFT, KMC, Microkinetic modeling	T = 500–800 K (TPD)	Effect of bimetallic catalyst on ammonia decomposition reaction using computational methods
27	[91]	O	Pt, Pd, Rh	DFT, TST, Microkinetic modeling	T = 500 K, 1000 K	Analysis of different catalyst surfaces for ammonia oxidation process (Pd most active, Pt most selective towards NO)
28	[77]	S	Transition metals Re stripe on Cu	DFT, Microkinetic modeling	T = 600–673 K P = 25–100 bar	Research of ammonia synthesis mechanism over dissociation of nitrogen using transition metal catalyst with at least 2 isolated reactive atoms
29	[56]	S	Fe3/θ -Al_2O_3	DFT, Microkinetic modeling	T = 300–1000 K P = 1–100 bar	Ammonia synthesis over Fe3/θ - Al_2O_3, comparison between dissociative and associative mechanism
30	[76]	S	HCP and FCC Co structures	DFT, Microkinetic modeling	/	Ammonia synthesis reaction modelled on Co catalyst
31	[66]	D	Ru (0001), Ru (1 1 1), Ir(1 1 1)	DFT, Microkinetic modeling, Batch reactor simulation	T = 400–600 K	Ammonia decomposition investigation over Ru and Ir using DFT calculations, microkinetic modeling and batch reactor simulation
32	[81]	S	Metals in plasma (Fe, Ru, Rh, Co, Ni, Pt, Pd)	DFT, Microkinetic modeling	T = 473 K − 673 K P = 1–100 atm	Vibrational excitation of N_2 molecule, plasma catalysis
33	[90]	O	Pt (1 0 0)	DFT, TST, Microkinetic modeling	T = 300–1200 K	Mechanism of ammonia oxidation process was determined, using DFT, TST, Microkinetic modeling
34	[60]	S	Ru (0001)	DFT	T = 300–350 °C	DFT calculation used for ammonia synthesis reaction mechanism and alkali metal promotion research
35	[53]	S	BCC Fe	DFT, Microkinetic modeling	T = 700 K P = 100 bar	BCC Fe nanoparticle construction to observe ammonia synthesis process over Fe catalyst, nanoparticle size, intrinsic activity and surface area are investigated
36	[63]	S	Ru-Co	DFT, Microkinetic modeling	Haber-Bosch conditions	Ru-Co catalyst investigation and comparison with Ru catalyst, reaction mechanism and catalyst investigation
37	[26]	S	Co_3Mo_3N	DFT	/	Precise mechanism description, Langmuir-Hinshelwood and Eley-Rideal mechanism, role of surface defects in mechanism and reaction conditions
38	[94]	S	MX - two-dimensional inorganic material (W2N)	DFT, Microkinetic modeling	T = 400–1400 K (models) P = 1 bar	Research of Mxenes used as a catalyst in nitrogen molecule dissociation in ammonia synthesis reaction
39	[95]	S	Re-Co alloys	DFT, Microkinetic modeling	T = 800 K P = 30 MPa	Correlation between Re Co alloys was established, effect of adsorbed nitrogen atom, rate determining step is described
40	[51]	S&D	Fe, Co, Ni, Cu, Ru/Mg Al_2O_4, Co_3Mo_3N	DFT, Microkinetic modeling	T = 773 K (measurements) P = 1 bar	Researching why optimal catalyst for ammonia synthesis reaction is not optimal catalyst from ammonia decomposition reaction
41	[52]	S	Fe (1 1 1)	DFT, KMC	T = 673 K (experiment) P = 20 atm (experiment)	Mechanism of ammonia synthesis reaction was investigated, reaction was modelled over Fe (1 1 1) and put to the test
42	[96]	D	CoCeAlO	Kinetic modeling, CFD	T = 550 °C	Ammonia decomposition in flat plate microreactor, kinetic modeling and computation fluid dynamics
43	[97]	D	V-based membrane	CFD	T = 300 °C P = 7.8 bar	CFD model of membrane reactor for H2 production from NH3

(no of NH_3/(total no. of NH_3 and N_2H_2)) with 10 nm nanoparticles due to lowest N_2H_2 generation.

DFT + microkinetic. A multiscale model of the reaction over a Ru/Ca_2NH catalyst was constructed by Nakao et al. [62], who included DFT calculations to determine the reaction mechanism and microkinetic modelling to pinpoint kinetics and the rate determining step. The model showed that combining Ru with a hydride/electride catalyst decreases the activation energy for N_2 bond cleavage due to the electron electron injection from the support. Since N_2 dissociation is the RDS, this increased the reaction rate and expedited the NH_x formation from lattice H^-.

Co doping as a promising way to increase the efficiency of Ru catalysts was studied by Benisalman et al. [63] with DFT calculations and microkinetic modelling over Ru-Co and Ru. They compared the Ru-Co catalyst with Ru, described the reaction mechanism and determined the optimal process conditions as well as studied the catalytic surface during the reaction. Nitrogen dissociation as the rate determining step occurs on Ru-Co due to more favourable N_2 binding to strong active Ru sites on account of electron donation from Co. Furthermore, Benisalman et al. [63] observed a high rate of catalyst poisoning by the hydrogen when the partial pressure of hydrogen exceeded 987.9 atm.

Another aspect that has to be considered using Ru catalysts is the toxicity of Ru. [64].

4.2. Ammonia decomposition

While ammonia synthesis has a major importance in the production of fertilizers, its reverse reaction (ammonia decomposition) is important when used as chemical (long-term) H_2 storage for fuel cells, electricity, heat production etc. It should also be noted that ammonia itself can be a poison if sufficiently concentrated. This is particularly important when ammonia is used as hydrogen source, which is often presented as a pollutant-free source (only true if ammonia is stored correctly and there are no uncontrolled ammonia emissions).

DFT. Reaction mechanism of ammonia decomposition was studied by Zhou et al. [65], who modelled it over Ru clusters anchored on carbon nanotubes using DFT modelling. Focusing on the rate limiting step and the size effect, they proposed following mechanism [65]:

$$NH_3^* + * \rightarrow NH_2^* + H^* \quad (1)$$

$$NH_2^* + * \rightarrow NH^* + H^* \quad (2)$$

$$NH^* + * \rightarrow N^* + H^* \quad (3)$$

$$H^* + H^* \rightarrow H_2 + 2* \quad (4)$$

$$N^* + N^* \rightarrow N_2 + 2* \quad (5)$$

Energy barriers on Ru@CNT were lower than on CNT, including the rate-determining step of nitrogen recombination.

DFT + microkinetic modelling. Kinetics and the favourable adsorption sites for ammonia decomposition were investigated by Lu et al. [66] using DFT calculations and microkinetic modelling to determine the mechanism over Ru (1 1 1), Ru (0001) and Ir (1 1 1). Batch reactor simulations indicated that hydrogen starts to form at 400 K on Ru (1 1 1), 425 K on Ru (0001) and 600 K Ir (1 1 1), which was confirmed by experiments. Ammonia adsorbed mostly on top sites, followed by bridge and hollow sites. Nitrogen recombination was found to be the rate-determining step.

Deshmukh et al. [67] described a detailed mechanism of ammonia synthesis and decomposition on the Ru catalyst. Using the transition state theory [68] and density functional calculations, they were able to determine key steps in both reactions. Furthermore, with the use of computational fluid dynamics (CFD) they designed a microreactor for hydrogen production from ammonia and studied the effect of geometric factors on the ammonia conversion over Ru/Al_2O_3. This makes it one of very few several levels encompassing microkinetic modelling studies.

DFT + KMC. Hellman et al. [69] used first-principles calculations to study ammonia synthesis and decomposition reaction over a Ru catalyst (Ru (0001) and Ru step). First-principles calculations at the DFT level supplied the input for the kinetic Monte Carlo simulations, where they observed the rate-limiting steps. Comparing their results with experimental data, a semi-quantitive agreement for the productivity was observed, as shown in Fig. 6 [69].

Prasad et al. [70] studied ammonia decomposition over the γ alumina supported Ru catalyst using a microkinetic model and DFT to calculate the activation energies and kinetic Monte Carlo for pinpointing the optimal experimental condition. Furthermore, Prasad et al. [71] studied ammonia decomposition for fuel cell applications over $Ru/\gamma-Al_2O_3$ in fuel cell relevant operating conditions. The purpose of their work was also finding rate determining step, which ended up being nitrogen adsorption/desorption step. Prasad et al. [72] further investigated ammonia decomposition reaction over $Ru/\gamma-Al_2O_3$ and developed a novel approach for experiments design, which included multiscale modelling of a fixed bed reactor. Monte Carlo was used in operating space to manipulate different variables such as pressure, temperature, residence time, catalyst surface area per reactor volume unit as well as gas inlet composition of reactants and products. The authors demonstrated the use of kinetic models, sensitivity analysis and informatics in catalytic systems for ammonia decomposition. Hence, multiscale microkinetic models were applied to the macroscopic process for improvements and guided catalyst design.

DFT + CFD. On the larger scale, for microreactors or reactors, ammonia decomposition has been extensively modelled. Deshmukh et al. [67] first modelled the detailed reaction mechanism using TST, bond order conservation technique (BOC) and DFT. This was coupled to a microreactor, which was described using computational fluid dynamics (CFD), to study the effect of geometric factors in the reactor. It was found that adding catalytic posts reduces mass transfer effect and increases conversion. Furthermore, various shapes of posts do not affect the actual conversion but change the flow in the reactor, and thus the pressure drop in the reactor.

Deshmukh et al. [73] also coupled propane combustion with ammonia decomposition reaction over a Ru catalyst for the production of CO-free hydrogen. Using CFD to model the microreactor, they studied a system where both reactions happened at the same time in the counter current flow. Propane combustion reaction provided a sufficient amount of heat needed for ammonia decomposition reaction. For the optimal conversion, both flows had to be precisely balanced due to the excessive energy produced by propane combustion. Another reactor was designed by Schumacher et al. [74] who also studied ammonia decomposition reaction and oxidation reactions. Using CFD, they designed an autothermal microchannel reactor for ammonia decomposition reaction, which showed an acceptable accuracy compared to the experimental data. Experimental work and CFD simulations were done by Chiuta et al. in order to obtain hydrogen production using commercial Ru/Al_2O_3. [75].

4.3. Using transition metals

4.3.1. Ammonia synthesis

DFT + microkinetic simulations. In addition to Fe and Ru, several other transition metals have been studied when searching for improved catalysts for ammonia synthesis, decomposition or ammonia oxidation. Ammonia synthesis was studied by Zhang et al. [76] over Co HCP and FCC structure. Researchers used DFT calculations and microkinetic simulations to compare Co structures and found out that Co HCP structure shows higher activity for nitrogen molecule dissociation, which is also the rete determining step in dissociative mechanism of ammonia synthesis.

Singh et al. [77] used DFT calculations and microkinetic modeling to study NH3 synthesis on active sites requiring the dissociative adsorption of N atoms. They found that “on-top” binding of nitrogen showed improved scaling behaviour, leading to higher predicted activity. Stabilizing such active sites could enable thermochemical ammonia synthesis under more favourable conditions.

Several transition metals were researched and plotted against the volcano curve (Fig. 7) by Jacobsen et al. [78], who used DFT calculations and microkinetic modeling. As the volcano peak varied depending on the reaction conditions, the authors showed that ammonia synthesis is strongly dependent on the binding energy of the catalyst, as epitomised by the Sabatier principle.

Yin et al. [79] screened several transition metal complexes (Sc, Cu, Mo, Ru, Rh, Pd, Re, Ir, Pt) using first-principles calculations. In terms of stability, electrical conductivity, Pt embedded in monolayer g-C_3N_4 was chosen as the most promising candidate and further investigated using DFT and molecular dynamics. Platinum (Pt)/g-C_3N_4 was found to be particularly active at room temperature (limiting potential of −0.24 V), with excellent stability and NRR selectivity due to the predominant adsorption of N_2 over H. The Pt atom and g-C_3N_4 work together to provide active sites for NRR.

Tackling the high energy consumption for ammonia production, Wang et al. [80] theoretically screened several transition metals (Cu, Ag, Au, Ni, Pt, Pd, Rh, Ir (FCC), Co, Ru, Re and Os as HCP structures and Fe, Mo and W as BCC structures) to increase the catalyst activity, selectivity,

reaction rate and reactive species stability. After using DFT calculations and confirming the superior activity of Fe and Ru, different surface geometries were tested and step sites of the catalysts were found to possess a higher activity in comparison to the terrace sites. Furthermore, confined terrace sites on Co were found to outperform the Ru catalyst two- to three-fold due to a lower barrier for N_2 dissociation. Thus, confined catalytic sites, which are reported to be difficult to manufacture [48], can seriously improve ammonia synthesis rate even when few are present.

Mehta et al. [81] investigated ammonia synthesis through vibrational excitation of nitrogen in a plasma. Using DFT and microkinetic modelling authors predicted it is possible to produce ammonia using non-thermal plasma at low temperatures and atmospheric pressure at rates that match thermal catalytic systems for ammonia production. They also explained that catalysts used with plasma are not same as for thermocatalytic processes, since they need to bind nitrogen more weakly. They confirmed their predictions by kinetic experiments in plasma reactor. For a comprehensive review of plasma-related ammonia synthesis reactions, the reader is referred to the review by Rouwenhorst et al. [82].

4.3.2. Ammonia decomposition

DFT + microkinetic simulations. Analogously, transition metals are active for ammonia decomposition. Hansgen [83] studied several metals (Co, Pd, Pt, Ni, Ru, Rh, Ir, Re and Mo) and identified the most promising monolayer bimetallic system, using DFT calculations and microkinetic modeling, as a Ni-Pt-Pt (1 1 1) surface, which is a monolayer of Ni atoms on a Pt (1 1 1) substrate. Bimetallic surfaces were also studied experimentally, using temperature-programmed desorption and high-resolution electron energy loss spectroscopy. Their experimental results predicted that Ni-Pt-Pt catalyst can be even more active than Ru catalyst (steady state decomposition under 600 K, occurred at temperatures of 325 K). They also showed that the activity of the catalyst is highly dependent on the location of Ni adsorbed on the surface.

Xie et al. [84] developed a high entropy alloy (HEA) catalyst from earth abundant as CoMoFeNiCu nanoparticles. The catalyst was catalytically active due to a robust tuning of surface adsorption properties and stable under the reaction conditions. The energies were obtained using DFT and coupled to atomistic modeling of the HEA nanoparticles to check the phase stability with Monte Carlo simulations. There was little variation between the nanoparticle structure at three different temperatures (573 K, 750 K and 1000 K), hinting at high stability under different conditions. It was shown that the catalyst benefited from the robust tuning of the Co/Mo ratio and that it overcame the miscibility limitations from conventional bimetallic Co-Mo catalysts. Wang et al. [85] also investigated ammonia decomposition over Co, Fe and Co-Fe catalysts using a mixed theoretical and experimental approach. In their investigation, they conducted TAP (temporal analysis of products) experiments, uniquely incorporating simultaneous pulsing of reactants and products to discern the lifetimes of various products. Furthermore, they applied quantum mechanical calculations to interpret their results, ultimately identifying an enhanced performance in the bimetallic CoFe catalyst.

He et al. [86] looked into clean, oxygen- and hydroxyl-predosed Ir (1 0 0) using DFT and microkinetic analysis, evaluating the adsorption stability and site preference for ammonia and its derived species. Furthermore, they determined the minimum energy paths for each elementary step. Ammonia desorption and dissociation were found to be competitive on clean Ir (1 0 0) surfaces, while ammonia dehydrogenation is affected by -O and –OH groups. The preadsorbed species activate the dehydrogenation of NH and NH_3 but inhibit the transformation of NH_2.

DFT + KMC. Guo et al. [87] used DFT and KMC modeling for patched bimetallic surfaces in ammonia decomposition. Using a submonolayer of Ni on Pt and comparing it to an ideal monolayer Ni-Pt-Pt and pure Ni on Pt, an almost two magnitudes higher activity was seen due to bifunctionality. It was shown that Ni terrace sites catalyse the N–H bond scission, while (0 0 1) edges catalyse the nitrogen molecule association. Ni and Pt were also combined by Nunez et al. [88] and studied with Monte Carlo and DFT calculations to ascertain the interplay between the terrace sites and step sites of defected Ni adlayers on a Pt substrate. An optimal structure was proposed to contain high amounts of step and terrace sites close together, showing a five-fold increase in activity in comparison to randomly generated structures.

DFT + KMC. The performance of Ni/Pt structures was further studied by Guo et al. [89], who used DFT and KMC to investigate Ni clusters with various sizes and shapes on Pt (1 1 1). They found out that for nitrogen near steps association barriers are lower in comparison to terraces, and showed the importance of steps of Ni cluster on Pt (1 1 1) for nitrogen molecule desorption. Their models showed that the actual decomposition of ammonia happens on Ni due to stronger adsorption.

4.3.3. Ammonia oxidation

DFT + microkinetic modelling. Ammonia oxidation is also catalysed with transition metals. Novell-Leruth et al. [90] looked into the reaction over Pt(1 0 0) studying the mechanism and kinetics using DFT calculations and microkinetic modeling. Using TST they were able to determine the rate constants of the elementary steps, which identified NO desorption as the rate limiting step. The microkinetic model was found to predict the product distribution well at various temperatures and different O_2/NH_3 ratios.

Pt, Pd, and Rh were also studied by Ma et al. [91] with DFT calculations and microkinetic modelling. Platinum group metals are important in catalyzing ammonia slip, but their rates and selectivities differ. Rh and Pd showed lower NH_3 oxidation rates but greater selectivity to N_2 than Pt. The authors found out that a dual-layer catalyst of Pt and zeolite-based SCR catalysts can increase N_2 selectivity but reduce the overall rate. Combining Pt with Rh or Pd may achieve similar performance. Pd and Rh may also be beneficial in reducing the formation of N_2O in the Ostwald process. The authors conclude that the surface coverage also affects product selectivity, and searching for catalysts with high NO(g) formation barrier and low N_2 (g) formation barrier can increase N_2 selectivity.

Ni is another promising transition metal used for ammonia decomposition or oxidation. Studying Ni(1 1 0) with DFT and microkinetic modelling, Duan et al. [92] determined the elementary steps of the reaction and identified NH_2^* as the most important intermediate. Comparing several surfaces, Ni (1 1 0) was more active than Ni (1 1 1) and Ni (2 1 1).

DFT + MD + lattice dynamics. Moon et al. [93] further investigated structural transformations of Ni/Ba H_2 during the nitridation and hydrogenation steps during ammonia synthesis. Building an extensive multiscale model, which included first-principles calculations, molecular dynamics and lattice dynamics to understand and better interpret neutron spectroscopy results, structures and dynamics, ball milling process was found to be the key element in ammonia synthesis. It can reduce Ba H_2 crystalline size and potentially increase its reactivity in ammonia synthesis reaction.

5. Multi-element formulations

As nitrogen dissociation is the rate-determining step in ammonia synthesis, great effort is exerted towards finding formulations that lower the required activation barrier. Gouvenia et al. [94] used a model comprising of DFT and microkinetics to study MXenes, which are a class of two-dimensional inorganic material and can adsorb and dissociate N_2 at milder conditions. Furthermore, they suggested using MXenes as a support to transition metal-based catalyst, forming ‘‘double’’ catalysts able to catalyse the reaction at less harsh Haber-Bosch process conditions.

Zeinalipour-Yazdi et al. [26] investigated the reaction mechanism

over Co_3Mo_3N at the DFT level, studying the Langmuir–Hinshelwood dissociative mechanism and Eley–Riedel associative reaction mechanism. Both dissociative and associative reaction mechanisms are presented in Scheme 1 and Scheme 2. It was shown that ammonia can be synthesized over Co_3Mo_3N at milder conditions following the ER mechanism when impinging hydrogen reacts with the adsorbed nitrogen. Investigating how surface defects affect the required reaction conditions, they were found out to speed up the reaction at milder conditions.

Re-Co alloys were studied by Cholach et al. [95] using DFT and microkinetic modeling. ReCo (0001) alloys as well as Co-supported single and dual Re atoms were modelled to determine the effect of electron donation from the Co (0001) support. A flat Fe (1 1 1) plane was also studied for comparison with existing experimental data to ascertain the models' reliability. Describing the correlations between Co, Re and the adsorbed nitrogen atoms, it was shown that Re_3Co and $ReCo_3$ exhibit maximum catalytic activity under the specific reaction conditions with nitrogen hydrogenation as the rate-determining step.

Maleki et al. [96] investigated ammonia decomposition reaction over CoCeAlO in a flat plate microreactor using kinetic modeling and CFD to design a microreactor for hydrogen production. Some kinetic experiments were also carried out with the changing temperature and ammonia flow to benchmark the simulation data, showing a good agreement (Fig. 8 shows ammonia conversions at various flow rates and reaction temperatures). The authors concluded that the reactor working at the highest rate results in ideal ammonia decomposition reaction since the microreactor aspect ratios were optimal and had no mass transfer limitations. It was proposed that the same experimental and modeling approach could be used to design a fluid–solid reaction system.

Computational fluid dynamics for ammonia decomposition reaction was also performed by Hla et al. [97], who studied a membrane reactor. They investigated the performance of the reactor for the hydrogen production. From 3D CFD model, researches obtained hydrogen production rates from 4.6 kg/day to 11.6 kg/day, depending on the reaction conditions. Furthermore, they investigated the hydrogen separation process from $H_2/N_2/NH_3$ mixture.

Table 1 provides a condensed overview of studies focused on the multiscale modeling of ammonia synthesis and decomposition. It allows for a comparison of various catalysts, reaction conditions, and multiscale methods employed in these researches.

6. Conclusion and future outlook

Ammonia synthesis and decomposition reactions have had a profound effect in the last 100 years since the discovery of the Haber-Bosch process. Despite a long history of research, the catalyst development and process optimisation are still pertinent research topics since ammonia production requires large amounts of energy and any improvements have multiplicative effects. Multiscale modeling and process design are becoming increasingly important as they can describe the set up before experimental work is carried out.

Although various catalysts have been tested for ammonia reactions, the first-generation Fe catalysts remain prevalent due to their low price and reasonable efficiency. Second-generation Ru catalysts and other transition metals are used less commonly due to high price as Ru is a critical raw material. In this work, we reviewed all of them. In all cases, multiscale approaches containing the atomic scale, (DFT) meso scale (KMC, Microkinetic modeling) and reactor scale (CFD) are considered. The typical combinations are coupling DFT and the meso scale or coupling microkinetic modelling with CFD. There are no full-fledged multiscale models that would encompass all reaction scales.

In the field of ammonia synthesis and decomposition, we have showcased the usefulness of multiscale modeling. By employing DFT calculations, we can accurately examine the electronic interactions between adsorbate and catalyst surface, thereby determining the most effective catalyst for ammonia synthesis. Our review encompasses DFT calculations of ammonia reactions across diverse catalysts, ranging from the benchmark Fe catalyst to various transition metal catalysts. Microkinetic modeling is integral to this process, as it accounts for the reaction conditions. Specifically, the DFT output is utilized in microkinetic modeling to investigate the specific reaction mechanism over a catalytic system previously defined in DFT. The multiscale process culminates with the design of a reactor that incorporates heat and mass transfer. Moreover, we have illustrated the implementation of multiscale modeling in ammonia synthesis and decomposition reactions.

Given the indispensability of fertilizers in our lives and the substantial energy consumption associated with the ammonia synthesis process, ammonia synthesis will continue to be a popular area of investigation. The numerous studies focused on ammonia-related issues are beneficial in addressing the energy consumption concerns. By adopting a multiscale modeling approach, we can achieve greater results in a shorter timeframe. In addition, researchers are exploring novel methods of ammonia synthesis in electro and plasma catalysis to produce greener ammonia.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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