Computational chemistry for NH₃ synthesis, hydrotreating, and NO_x reduction: three topics of special interest to Haldor Topsøe

Ahmed O. Elnabawy, Srinivas Rangarajan, Manos Mavrikakis*

Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415
Engineering Drive, Madison, WI 53706, USA

*corresponding author; email address: manos@engr.wisc.edu

Abstract

Computational chemistry, especially density functional theory, has experienced a remarkable growth in terms of application over the last few decades. This is attributed to the improvements in theory and computing infrastructure that enable the analysis of systems of unprecedented size and detail at an affordable computational expense. In this perspective, we discuss recent progress and current challenges facing electronic structure theory in the context of heterogeneous catalysis. We specifically focus on the impact of computational chemistry in elucidating and designing catalytic systems in three topics of interest to Haldor Topsøe, namely, ammonia (NH₃) synthesis, hydrotreating, and NO_x reduction. We then discuss the common tools and concepts in computational catalysis that underline these topics and provide a perspective on the challenges and future directions of research in this area of catalysis research.

Keywords: NH₃ synthesis, hydrotreating, NH₃-Selective Catalytic Reduction (SCR), transition metals, transition metal sulfides, volcano plots, DFT

1. Introduction

Haldor Topsøe, over the last several decades, has promoted fundamental research in heterogeneous catalysis that has, in turn, contributed to the development of an array of commercial catalysts in chemical synthesis, petroleum refining, and emission control. Here, as a tribute to his memory, we discuss the state-of-the-art in computational catalysis and its contribution to the field through illustrative examples in three areas. Specifically, we discuss how electronic structure theory has enabled an atomic scale understanding of NH_3 synthesis, hydrotreating and NO_x removal in terms of (i) identifying active sites, (ii) elucidating reaction mechanisms, effect of support, and role of promoters, and (iii) designing catalysts with improved activity and selectivity. Further, in each of these examples, we highlight the complementary role of experiments and theory, which has been a key characteristic of the research inspired by Haldor Topsøe; we discuss, in particular, instances of theoretical predictions that have been corroborated by advanced characterization techniques (e.g. catalyst morphology in hydrotreating) and experimental observations rationalized by theory (e.g. role of promoters and nature of active sites for NH_3 synthesis).

We begin by discussing the current understanding and open challenges of: NH_3 synthesis on transition metals, hydrodesulfurization on transition metal sulfides, and NO_x removal on zeolites, transition metal oxides and noble metals. While each example is in itself large enough to have dedicated reviews, and several such reviews are available [1-5], our effort here is to showcase some of the principal insights and outcomes derived from computational catalysis. A common suite of theoretical concepts and tools underline these three case studies, which is a subset of the growing lexicon of computational catalysis – electronic structure calculations mainly using density functional theory (DFT), ab initio thermochemistry [6], microkinetic

modeling, and a host of semi-empirical structure-property correlations derived from theoretical calculations such as linear scaling [7] and Brønsted-Evans-Polanyi relationships [8]. We, therefore, present our perspective on the concurrent application of these concepts and tools towards an improved mechanistic understanding and the identification of improved heterogeneous catalysts.

2. Catalysis of Ammonia Synthesis

NH_3 is mainly used as a fertilizer; it is the second most commonly produced chemical in the world, with an annual global production capacity exceeding 200 million metric tons [9], and an estimated market of 102 billion dollars in 2019 [10]. Additionally, NH_3 synthesis has also been traditionally considered a model heterogeneous catalytic reaction both from pedagogical viewpoint and from the standpoint of advancing and testing methods and concepts in catalysis. Although N_2 is abundant in Earth's atmosphere, its strong triple bond (9.8 eV [11]) makes its activation challenging. Early attempts in nitrogen fixation tried to mimic lightning to stimulate gas phase production of NH_3 which propagates through radicals formation [12].

The Haber-Bosch process – the current means for mass-production of NH_3 – operates at around 700 K and up to 300 bar, which makes it responsible for the consumption of around 2% of the world's energy production [13]. The high temperature makes kinetics faster, but reduces the equilibrium conversion because NH_3 synthesis is exothermic, whereas the high pressure shifts the equilibrium towards the product [14]. Iron is the common choice of catalyst; although ruthenium is more active [15,16], it finds limited industrial application because it is more expensive and unstable under reaction conditions [17]. Haldor Topsøe's interest in catalytic NH_3 synthesis has played a central role in driving important advances in understanding this chemistry in greater depth. We begin this section by discussing the mechanism of NH_3 synthesis by

exploring the free energy landscape at high temperature and pressure. Subsequently, we will briefly discuss computational catalysis studies that have explored the structure sensitivity of the reaction and the effect of support, promoter, and strain. We finally describe recent research efforts in NH_3 synthesis, specifically, the pursuit of a low-temperature low-pressure NH_3 synthesis process.

2.1. Mechanism

Figure 1 [18] below depicts the free energy surface of a widely accepted mechanism of NH_3 synthesis on stepped ruthenium surfaces. The mechanism shown in panel (c) assumes N_2 dissociation to be the rate-limiting step [14,18-22], with all other steps being quasi-equilibrated [17-20,23,24]. Panel (a) indicates the thermodynamic feasibility of NH_3 synthesis at ambient temperatures; the process has a net negative free energy change. The kinetics is much less favorable, however, since the catalyst surface will be overwhelmingly covered by the reaction intermediates due to their strong adsorption energies. Higher temperatures increase the rate of reaction but also render the overall thermochemistry less favorable. To keep ΔG negative, higher pressures are required as shown in panel (b).

Figure 1 Free Energy Surface for NH_3 synthesis at different pressure and temperature conditions, a stoichiometric feed of reactants, and a fixed NH_3 pressure of 1 bar. Free energies are calculated using ideal gas and harmonic vibrational approximations. Reprinted from Chemical Physics Letters, 598, Vojvodic et al., “Exploring the limits: A low-pressure, low-temperature Haber-Bosch process”, 108-112, (2014), with permission from ELSEVIER [18]

Panel (a) shows that the barrier of step 1 (N_2 dissociation) is directly related to the stability of the intermediate (N^*) formed. In general, the more stable N^* is, the lower the N_2 dissociation barrier. Such a relationship, known as a Brønsted-Evans-Polanyi (BEP) correlation, has been shown to exist for NH_3 synthesis in several DFT studies [15,18,19,25]. These correlations describe the electronic effects of different metals, however, they are also affected by geometric factors as depicted in figure 2 [15], wherein the line for the open facets lies below that for the close-packed surfaces; open surfaces, therefore, present lower activation energy barriers. While lowering the barrier for N_2 dissociation – the rate determining step – can increase the rate, this comes at the expense of turnover of the catalytic cycle due to the occupation of the surface by strongly bound reaction intermediates as inferred from the BEP correlation.

Figure 2 A model BEP correlation for activation energy of N_2 dissociation versus the adsorption energy for two nitrogen atoms. All energies are relative to N_2 gas. Black circles correspond to close-packed surfaces, while red triangles correspond to open facets and stepped surfaces. The inset shows a schematic of the N_2 dissociation energetics. Reprinted from Applied Catalysis A: General, 222, Dahl et al., "Electronic factors in catalysis: the volcano curve and the effect of promotion in catalytic NH_3 synthesis", 19-29, (2001), with permission from ELSEVIER [15]

2.2. Structure sensitivity

NH₃ synthesis on Fe and Ru is widely accepted as a model depiction of the effect of surface atomic topology and catalyst morphology on the macroscopic turn-over frequency (TOF) and observable rates [21,25]. For instance, Nørskov and coworkers, using DFT, observed a restructuring of the surface of a Ru(0001) upon the dissociative adsorption of N₂, which infers structure sensitivity [26]. A combined theoretical and experimental approach has shown the dissociative adsorption of N₂ on Ru(0001) to be totally dominated by the step sites rather than the terraces, with a difference in activation energy barrier of 1.5 eV [27]. The structure sensitivity of Ru(0001) has been corroborated by experiments. For example, Dahl et al. [21] used temperature programmed desorption (TPD) to study dissociative adsorption of N₂ on Ru(0001). The authors argued that a drop in the coverage of atomic nitrogen in the vicinity of step sites of Ru(0001) upon decoration by gold (a noble metal) suggests the dominant role played by these sites in NH₃ synthesis. The reason behind the enhanced activity of step sites is twofold: i) an electronic effect due to intrinsic low-coordination, which brings the d-band center [28] of the step-edge sites closer to the Fermi level, and ii) a geometric effect where adsorbates find highly favored sites for stable adsorption and fast reaction, with the geometric effect being more pronounced [20,21,27]. Comparing the DFT calculations of activation barriers of N₂ on step and terrace sites reveal the geometric advantage the steps offer. On the steps, the two nitrogen atoms produced by the N₂ dissociation will not have to share a single Ru atom, since five Ru atoms (so-called B₅ type-sites) are part of the activated complex on the step instead of four Ru atoms on the terrace [27]. The destabilizing effect of sharing surface Ru atoms in the activated complex has been revealed by DFT to be the result of a downshift in the d-band of the Ru atom by one of the nitrogen atoms, rendering the interaction of the same Ru atom with the second nitrogen atom

rather weak [26]. The B5-type sites model has been used to explain experimental observations where larger Ru particles - up to some limit - are found to be generally more active than smaller ones (e.g. smaller than 0.7-0.8 nm in size), as larger particles expose more of the B₅-type sites [29-31]. Similarly for Fe, larger particles and the (111) facet show higher TOF for they expose larger number of C7 sites (atoms having seven neighbors) [32,33].

2.3. Promotion effects

Both Fe and Ru are known to be amenable to promotion in NH₃ synthesis, with Ru being, in general, more sensitive to promoters [17]. As a rule of thumb, the extent of the promotion effects in general increases with the atomic number of the promoter alkali metal [34]. For example, DFT calculations have shown that depositing 1/6 ML of Cs on Ru(0001) could decrease the barrier for N₂ dissociation on the steps by 0.29 eV, compared to 0.13 eV for 1/8 ML of Na [35]. It has been shown experimentally that cesium [36] and barium [36,37] are among the best promoters for NH₃ synthesis over Ru. DFT calculations has been used to gain an atomic-level understanding of the effect of promotion. These calculations have suggested that the promotion effect is two-fold: i) decreasing the barrier for N₂ dissociation; the rate-determining step for NH₃ synthesis, and ii) destabilizing surface intermediates, thus availing more active sites for turnover [15].

Promotion by alkali metals, from a theoretical viewpoint, has been generally described in the framework of electrostatics, where the electric field (ϵ) induced by the alkali metal interacts with the dipole moment (μ) of an adsorbed state via the relation [35,38,39]:

$$\Delta E_{\text{dipole}} = - \epsilon \mu$$

where ΔE_{dipole} is the electrostatic interaction between the alkali metal and the adsorbate. As far as the adsorbate is concerned, a more negative induced dipole moment indicates a lower barrier for

its dissociation [38]. This effect is induced by electron-donating electropositive elements, which tend to increase the surface's activity towards bond breaking. Adsorbates that donate negative charge to the surface (e.g. NH_x , $x=1-3$) are thus destabilized by the promoter; on the other hand, adsorbates such as atomic hydrogen H are unaffected by the presence of promoters [15,20].

Electronegative promoter elements would, in contrast, have adversary effects; for example, DFT calculations showed that the decoration of Ru(0001) with sulfur resulted in a higher barrier for N_2 dissociation due to Pauli repulsion and the strong interaction of sulfur with the 4d states of Ru. This weakens the binding of the activated complex with the surface and destabilizes the transition state [38]. Because not all promoters achieve the two tasks of promotion – lowering the N_2 dissociation barrier and destabilizing surface intermediates – equally, it is often a good idea to bring together two promoters that complement the functions of each other; and thus obtain an overall synergistic effect. This was demonstrated experimentally when a Ru catalyst was doped by Cs and Ba simultaneously, where Cs provides for the electronic effect which lowers the N_2 dissociation barrier, while Ba provides for a geometric effect that ultimately frees more of the active sites and makes them available to turnover [29]. There is, however, a limit, to the extent to which the complementary effects of the dopants can improve reactivity because the magnitude of reduction in activation barrier is constrained by the reaction energy [18].

2.4. Support effects

Supports often interact with the promoters adsorbed on the surface, thus inducing morphological changes. For example, Hansen et al. [40] combined HRTEM imaging and DFT studies [27] to conclude that the affinity of the promoter for a specific support can determine the amount of promoter near the active site. Another experimental study, by Jacobsen et al. [31], used

additional DFT results to attribute the decreasing activity trend in Ru on a variety of supports – $\text{Ru/MgAl}_2\text{O}_4 > \text{Ru/C} > \text{Ru/Si}_3\text{N}_4$ – to a concomitant decrease in the number of B₅-type sites.

2.5. Strain effects

DFT has played an instrumental role in demonstrating the increased surface reactivity upon lattice expansion, due to the up-shift of the metal d-states [28,41-44]. Strain effects have been demonstrated in NH_3 synthesis. N_2 dissociation was studied using DFT for an expanded lattice of fcc-Fe(111); the dissociation barrier decreased by 0.38 eV for a 4% increase in the lattice constant parallel to the surface [45]. At the same time, the stretched surface showed an increase in the binding energies of molecular and atomic nitrogen, in agreement with the BEP relationships [15,18,19,25,46]. As a result, the favorable effect of strain on the N_2 dissociation barrier was partially offset by a stronger binding of N, leading to an enhanced partial surface poisoning by N^* [19].

Strain effects, physically realized by depositing a pseudomorphic layer on top of a substrate metal having a larger lattice constant, have also been studied. For instance, Egeberg et al. [30] have combined DFT and experimental data for the system Fe/Ru(0001), whereby in addition to strain effects, the ligand effect reflecting the electronic coupling of the two metals at their interface, plays an important role in determining surface reactivity [47].

2.6. Open challenges

NH_3 synthesis is one of the most well-studied heterogeneously catalyzed reactions. There remains, however, the open challenge of mitigating the severe conditions required by the Haber-Bosch process. Biologically, NH_3 synthesis is catalyzed by the nitrogenase enzyme, which,

despite its need for a large energy input, proceeds at ambient conditions. This has inspired the pursuit of a man-made process that alleviates the high temperature and pressure required by the industrial process. Since nitrogenase uses protons and electrons in the process, this pursuit has traditionally been tackled in an electrochemical context [14,48,49].

DFT studies have shown that nitrogenase catalyzes NH_3 production via an associative hydrogenation mechanism in which hydrogen is directly added to the nitrogen molecule adsorbed on the active site, without dissociating N_2 [48]. This understanding can be extrapolated to the design of electrocatalysts that mimic the biological process. One step in this respect was made by Nørskov and coworkers [48] who combined BEP correlations, scaling relations, and the so-called computational standard hydrogen electrode [50] to construct volcano plots and to identify trends among transition metals for the electrocatalytic synthesis of NH_3 . Based on this analysis, flat surfaces of the early transition metals Sc, Y, Ti, and Zr were found to bind N adatoms more strongly than H adatoms, and thus suppress the competing reaction of H_2 evolution at the applied bias necessary for hydrogenation of adsorbed molecular nitrogen by protons. Finally, Nørskov and coworkers [18] have suggested that search for catalysts for a low-temperature low-pressure thermal Haber-Bosch process should focus on oxides rather than metals.

3. Catalytic Hydrotreating

Hydrotreating involves using hydrogen to remove sulfur (hydrodesulfurization, or HDS) from crude oil on nickel or cobalt promoted molybdenum sulfide catalysts to produce fuel such as ultra-low sulfur diesel (ULSD) containing less than 20 ppm S. Concurrently, the nitrogen in the feedstock is also catalytically removed (hydrodenitrogenation, or HDN). In the last twenty five years, and particularly in the last decade, computational catalysis has played a significant role, in

conjunction with experiments, for elucidating the atomic-scale location and role of promoters, the likely active sites, the effect of support, the mechanism of HDS for the thiophene family of molecules, and the inhibition by organonitrogen compounds in the feed [2,51,52]. Haldor Topsøe's interest in this research area has played a central role in driving related developments. In this section, we briefly discuss recent progress and present existing challenges in atomic-scale modeling of hydrotreating processes.

3.1. Catalyst structure

Density functional theory calculations have provided insights into the structure and plausible location of active sites in hydrotreating catalysts. Molybdenum sulfide (MoS_2) is a layered structure with each layer consisting of a trilayer of S-Mo-S. The edges of molybdenum sulfide particles – which can either be the metal (M or Mo) or sulfur (S) edge depending on the edge termination – have been long postulated to be location of active sites responsible for HDS. Using *ab initio* phase diagrams, several DFT-based studies have shown that under HDS conditions, the edges undergo substantial reconstruction [53-59]; the most recent studies [58-60] show that both edges, at HDS conditions, are decorated by sulfur and hydrogen atoms to varying degrees. Prodhomme et al. [58] showed that the formation of coordinatively unsaturated sites (CUS) on the metal edge and sulfur vacancy sites on the sulfur edge requires modest barriers (less than 0.8 eV), thus reaffirming the notion that these sites are responsible for catalysis.

Recent advancements in scanning tunneling microscopy (STM) have led to a direct corroboration of these predictions. For instance, DFT predicts that, under STM imaging conditions, the metal edges of a triangular shaped MoS_2 particle synthesized under sulfidative conditions will be saturated by sulfur dimers; Lauritsen et al. showed that this is also inferred from STM images [61]. Figure 3 shows the STM images of triangular (exposing only metal edges) and hexagonal

shaped (with sulfur and metal edges) MoS₂ particles obtained under different synthesis conditions. The bright “brim” along the edges of the catalyst particles correspond to metallic states, as predicted by DFT [59], and is purported to be active for HDS. Further, in agreement with Prodhomme et al. [58], CUS sites were seen on these nanoparticles where thiophene or benzothiophene could adsorb.

Figure 3 STM images of a triangular (A) and hexagonal (B) particles synthesized under sulfidative and sulfo-reductive conditions respectively. Line scans (C) show the differences in edge terminations in these clusters. Reprinted from *Journal of Catalysis*, 221, Lauritsen et al., “Atomic-scale insight into structure and morphology changes of MoS₂ nanoclusters in hydrotreating catalysts”, 510-522, Copyright (2004), with permission from ELSEVIER [61]

In early DFT studies by Raybaud et al. [62] and Byskov et al. [63], it was shown that nickel and cobalt promoters prefer the edges of the catalyst and that their lower metal-sulfur bonding increases the presence of unsaturated metal atoms. Recent analysis by Raybaud and coworkers [64] on predicting the morphology of nickel and cobalt promoted catalyst particles showed that

the promoters could partially or fully substitute molybdenum atoms at either edges although complete cobalt (nickel) promotion preferred the sulfur (metal) edge. Using Wulff construction, representative structures of promoted MoS₂ nanoparticles were proposed as shown in Figure 4. It can be seen that several additional types of sites – corner and NiMo/CoMo bridges – are created. STM has also recently been used to verify the location of nickel and cobalt promotion on the edges of the MoS₂ nanoparticles [65].

Figure 4 A representative set of possible CoMoS (a & b) and NiMoS (c & d) morphologies. Violet: Co, red: Ni, cyan: Mo, yellow: S. Arrows point to new mixed catalytic sites formed upon partial and full promotion of the edges. Reprinted from *Catalysis Today*, 130, Krebs et al., “Mixed sites and promoter segregation: A DFT study of the manifestation of Le Chatelier’s principle for the Co(Ni)MoS active phase in reaction conditions”, 160-169, Copyright (2008), with permission from ELSEVIER [64]

3.2. Mechanism of HDS

Several DFT studies have explored the adsorption and reaction of thiophene, benzothiophene, dibenzothiophene, and their derivative molecules on unpromoted molybdenum sulfide. Most of these studies focused on the role of CUS sites in sulfur extraction [66-68]. For example,

dibenzothiophene was shown to adsorb either upright through its sulfur on a bridge site or in a flat configuration, when two consecutive CUS sites are available. DFT studies by Moses et al. [60], on the other hand, showed that thiophene is activated on an equilibrium metal edge by the brim sites, thereby not requiring CUS sites; subsequently, the molecule undergoes hydrogenation and sulfur removal on both edges. A single vacancy on the sulfur edge, however, is required to activate the S-C bond scission on these edges. Both edges contribute to HDS synergistically with the metal edge catalyzing thiophene adsorption and hydrogenation and the carbon-sulfur bond being preferentially broken on the sulfur edge despite the low concentration of vacancies.

Larger organosulfur compounds, such as dibenzothiophene and their alkyl substituted derivatives, undergo desulfurization through the direct desulfurization (DDS) or the hydrogenation (HYD) pathways [69]. While dibenzothiophene prefers DDS, initiated by adsorption through sulfur, 4,6 dimethyldibenzothiophene, wherein the sulfur atom adsorption is hindered by two adjacent methyl groups, prefers HYD [70,71]. Recent STM studies with dosing of substituted dibenzothiophenes have shown that these molecules can adsorb on the brim sites while dibenzothiophene itself preferred corners but could adsorb on sulfur vacancies, again indicating the potential role of other non-CUS-like sites [72].

3.3. Support effects

The size of the MoS₂ catalyst particles, their edge composition, and the extent of stacking are affected by the strength of their interaction with the support [73]. A strong support reduces catalyst particle size and stacking, thereby increasing dispersion; however, it can also reduce catalytic activity by binding with the edge atoms through a Mo-O-M_S linkage (where M_S is the metal of the support). Early studies showed that sulfidation at higher temperatures improved catalytic activity of promoted molybdenum sulfide catalysts on alumina support [74]. It was

proposed that the higher temperature leads to a weakened interaction between the support and the catalyst nanoparticles, simply because Mo-O-Al linkages are broken. Nørskov and coworkers [75] studied this support-catalyst interaction using DFT wherein they modeled the Mo-O-Al link as Mo-OH to understand the effect that the Mo-O bond has on metal-sulfur bond strength. They found that the presence of Mo-O bonds polarizes the metal-sulfur bond, thereby increasing the energy for vacancy formation and decreasing the electron density on the brim sites. Raybaud and coworkers [58,76-78] considered the adhesion of Mo_6S_n clusters of varying levels of sulfur saturation on alumina and titania and showed that “ligand effects” – physical (van der Waal’s interaction and hydrogen bonding) and chemical (direct Mo-O- M_S) bonding – manifest to different extents on both supports leading to different levels of stabilization and catalytic activities. Joshi et al. [79] suggested that the strength of Mo-O- M_S bond, and hence the support interaction, can be characterized by the thiolysis/hydrolysis energy of model gas phase clusters of the form $\text{Mo}(\text{SH})_n\text{-O-M}_\text{S}(\text{OH})_m$.

3.4. Catalyst design

Identifying the ideal transition metal sulfide catalyst for HDS has been a subject of interest in computational catalysis and, consequently, attempts have been made to isolate the right descriptor that relates activity/selectivity with a bulk or surface property of the catalyst. Several early studies looked into the correlation of HDS activity of transition metal sulfides with the metal-sulfur bond energy (E_{MS}). Toulhoat et al. [80] and Toulhoat and Raybaud [81] showed (figure 5a) that metal-sulfur bond energy of the relevant catalyst structure under reaction conditions calculated from DFT or from experimental cohesive energies showed a Sabatier-like volcano curve for the rate of HDS of dibenzothiophene on a number of transition metal sulfide catalysts. Recently, Moses et al. [82] used a surface property, namely HS binding energy, and its

effect on two possible rate limiting steps (S-C scission or H₂S desorption) to show a similar volcano plot for the rate of HDS over a variety of transition metal sulfides (figure 5b). Both volcano plots show that there is an optimal point in terms of metal-sulfur bond energy or SH binding energy that maximizes HDS activity. Too large a value leads to increasing the barrier for H₂S desorption and the formation of CUS sites, while a small M-S/SH energy would mean that the reactants and intermediates bind weakly and S-C bond scission becomes difficult. The volcano plot can also be used to identify opportunities through alloying. For example, while nickel sulfides show a weak M-S bond and MoS₂ lies on the strong-binding slope of the volcano, NiMoS is close to the peak in terms of activity. Recently, Raybaud and coworkers [76] used this volcano to suggest that trimetallic sulfide – nickel promoted mixed molybdenum and tungsten sulfide – should be even higher in activity compared to NiMoS.

3.5. Open challenges

Computational catalysis has clearly contributed, in a significant way, towards understanding the nature of the active sites and the reaction mechanism in hydrodesulfurization. These insights, in conjunction with information from experiments, have helped in developing catalyst synthesis techniques to maximize the number of active sites, decrease deleterious support interactions, and improve HDS activity; new generations of catalysts, for example, have been developed by Haldor Topsøe A/S that reportedly have higher activity by exposing a larger proportion of brim sites [83]. Nevertheless, several open issues still remain in this field which require state-of-the-art and new modeling and experimental methods to be applied concurrently; we discuss some of these below.

First, a complete mechanistic understanding of HDS of relevant organosulfur compounds and concomitant HDN of organonitrogen compounds found in typical gas oil feedstock and the role

of different catalyst edges is still elusive. Understanding HDN assumes particular significance for ULSD applications because nitrogen significantly affects HDS activity of alkyl dibenzothiophenes that need to be desulfurized [84]. While several experimental studies on inhibition by nitrogen and a few DFT studies on adsorption of model organonitrogen compounds on unpromoted [85] and Ni-promoted molybdenum sulfide [86,87] have been carried out, the specific understanding of the active sites and the extent of competition by organonitrogen in the feed and HDN intermediates with organosulfur compounds is still lacking.

Second, an understanding of the effect of catalyst support and the extent of stacking of MoS₂ nanoparticles of realistic size and morphology on adsorption and reaction of organosulfur and organonitrogen compounds is required as most reported calculations have been performed on idealized edges with no support interactions. Third, while volcano curves have been proposed for hydrotreating based on simplified mechanisms and reactivity descriptors, rigorous catalyst design studies involving a comprehensive mechanism of HDS, HDN, and hydrogenation of real feeds are required.

Finally, other catalytic materials such as transition metal nitrides and phosphides and noble metal alloys need to be explored computationally for deep desulfurization in the presence of organonitrogen compounds. New theoretical developments, especially new functionals and methods [6,88-93], allow for accurately estimating properties of complex materials and large molecules including weak van der Waal interactions. The application of these methods is essential for HDS and HDN given the potentially significant weak interactions between large aromatic species in crude oil and hydrotreating catalysts [94].

(a)

(b)

Figure 5 (a) Experimental activity as a function of E_{MS} of transition metal sulfides, Reprinted from *Journal of Catalysis*, 216, Toulhoat et al., "Kinetic interpretation of catalytic activity patterns based on theoretical chemical descriptors", 63-72, Copyright (2003), with permission from ELSEVIER [81]; (b) The rate as a function of HS binding energy. The predicted rate per active site relative to RuS_2 is marked by the red line, the vertical red lines mark the HS binding energy of individual sulfide surfaces. Experimental rates relative to RuS_2 in [molecules/(g s)] are marked with diamonds for [ref 25 therein], circles for [ref 26 therein], plus for [ref 27 therein], squares for [ref 24 therein], Reprinted from *Springer, Catalysis Letters*, 144, 2014, 1425, "Trends in Hydrodesulfurization Catalysis Based on Realistic Surface Models", Moses et al., Fig. 3, Disclaimer is given to the publication in which the material was originally published, With kind permission from Springer Science and Business Media [82]

4. Catalytic NO_x reduction

Nitrogen oxides are considered major environmental pollutants. Being vented with flue gases, they always accompany any combustion process, be it stationary (which accounts for 40% of NO_x emissions) or mobile (accounting for 50%). They are the main sources of photochemical smog troubling atmospheric conditions in big cities, and affect water resources and soil in the form of acid rain, causing several health and ecological problems [95]. NO_x is composed mainly of NO, with smaller amounts of other oxides like NO₂ and N₂O [96]. The aim of NO_x abatement is to selectively reduce the oxides into N₂. This poses a difficult challenge for the catalyst because the reduction has to be carried out under oxidizing conditions typical in flue gases. In addition, water vapor and SO₂ present in flue gases pose further challenges for the catalyst in terms of stability and surface chemistry (e.g. water competes with NH₃ for adsorption onto the acid sites on vanadia/titania [96,97]).

Several catalytic technologies have arisen in response to the challenges posed by NO_x abatement; these include: three-way catalysts (TWC), lean NO_x traps, and selective catalytic reduction either by hydrocarbons (SCR-HC) or NH₃ (SCR-NH₃). However, TWC is ineffective for NO_x reduction in the oxygen-rich atmosphere of high-efficiency engines [98,99], lean NO_x traps mainly aim to store NO_x under lean conditions [100], and SCR-HC catalysts have not provided enough appealing performance in terms of activity and selectivity so far [101,102]. SCR-NH₃, on the other hand, has been one of the most successful technologies yet due to the development of highly active and selective catalysts for this process and due to the progress made in terms of NH₃ storage and desorption technology [98,103]. We, therefore, discuss this process in greater detail in this section.

Catalysts employed for SCR-NH₃ include zeolites, mixed oxides, and noble metals. Haldor Topsøe had been instrumental in motivating and encouraging scientific and technological advances in this field. In what follows we will focus on the recent progress made in this field, with particular emphasis on the role played by DFT.

4.1. Zeolites

Bifunctional metal exchanged (Fe and Cu) zeolites have been used for SCR-NH₃ wherein metals catalyze NO reduction and acid sites adsorb and activate NH₃ [95]. SCR-NH₃ on metal-exchanged zeolites has been recently reviewed [5]. DFT has aided the identification of the active site, and hence, the reaction mechanism on Cu-exchanged zeolites. Quite recently, Ribeiro and coworkers [104] have shown that Cu(II) exchange – Cu(II) is the precursor to active Cu species as suggested by operando X-ray absorption spectroscopy or XAS experiments – prefers six-membered rings of the chabazite structure. They further used a statistical simulation approach to calculate the Si:Al ratio necessary for maximizing the concentration of active sites, Cu(II), in the six-membered rings. Furthermore, Schneider and coworkers [105] showed, using DFT, that NO-assisted NH₃ decomposition accounts for Cu(II) to Cu(I) reduction accompanied by the generation of proximal Brønsted acid sites onto which NH₃ adsorbs in the form of NH₄⁺ ion. An NO₂ intermediate oxidizes Cu(I) back to Cu(II), and N₂ was suggested to be produced in both oxidation and reduction half-cycles in this redox chemistry.

4.2. Mixed oxides

The most commonly used mixed-oxide catalysts for industrial use are based on vanadium pentoxide mixed with molybdenum oxide or tungsten oxide, all supported on anatase titania. A generic mechanism for SCR-NH₃ on V₂O₅-based catalysts was proposed by Nan-Yu Topsøe through *in-situ* on-line Fourier transform infrared spectroscopy and a microkinetic analysis

[97,106]. In this mechanism, acid-catalyzed (on Brønsted acid sites, V-OH, formed mainly by interactions with the titania support [107]) and redox (on V=O species) reactions complement each other in the catalytic cycle shown in figure 6 [106]. The cycle starts with the adsorption of NH₃ on a Brønsted acid site (step 1) followed by its activation (step 2); gaseous or weakly adsorbed NO subsequently reacts with the activated NH₃ in step 3. This yields V⁴⁺-OH in step 4 together with a short-lived intermediate that rapidly decomposes into the SCR products (N₂ and H₂O) and releases V⁵⁺-OH species in step 5. Finally, the V⁴⁺-OH is oxidized back to V⁵⁺=O in step 6 and thus the cycle is closed.

This proposed mechanism has been further corroborated by a DFT study that shed light on the energetics of the different steps [108]. In essence, NH₃ was found to adsorb as an ammonium ion bound to two vanadyl (V=O) groups with ca. -110 kJ/mol, reflecting the acidic properties of the catalyst. This is followed by the reaction of ammonium with NO to form a NH₃NHO intermediate, the dehydrogenation of which to NH₂NO is considered to be the rate-determining step. The transition state of this dehydrogenation step was found to be stabilized by interactions of NH₃NHO with the surface V-OH and V=O groups, as well as the support. The decomposition of NH₂NHO is fast, in line with its experimental invisibility. The decomposition goes through a number of surface-catalyzed isomerization steps as well as hydrogen transfer steps – the so called “push-pull” mechanism – to facilitate the migration of H from VO-H group on the vanadia surface to the –NO group of NH₂NHO. This emphasizes the requirements for the redox properties of the catalyst. Another theoretical study corroborated the “push-pull” mechanism and the short lifetime of NH₂NO, although it suggests that NH₃NHO formation is the rate-determining step rather than its decomposition [109]. However, in summary, both studies are along the lines of the scheme depicted in figure 6.

Figure 6 A proposed catalytic scheme for SCR-NH₃ on vanadium pentoxide-based catalysts, from Science, 265, 5176, Nan-Yu Topsøe, "Mechanism of the Selective Catalytic Reduction of Nitric Oxide by NH₃ Elucidated by in Situ On-Line Fourier Transform Infrared Spectroscopy", 1217-1219, (1994). Reprinted with permission from AAAS [106]

4.3. Noble metals

Recent research has also focused on using noble metal-based catalysts for SCR-NH₃ to identify thermally stable alternatives that can operate within a wide range of temperatures. For instance, Doronkin et al. [110] identified Ag/ γ -Al₂O₃, among a set of materials including Ag/TiO₂, Ag/ZrO₂, Sn/ γ -Al₂O₃, and In/ γ -Al₂O₃, as a promising catalyst for NO reduction by NH₃ and concluded that both the metal and the support played complementary roles in the reaction. DFT calculations on the (111) and (211) facets of several noble metals corroborate the finding that Ag is a very promising catalyst as it does not bind intermediates of NO oxidation to NO_x (which are steps that come *en route* to NO-SCR) too strongly, as depicted in figure 7 [110]. H₂ is essential for the activity of these catalysts, as it assists with the removal of NO₃ from the surface of the catalyst. In an attempt to understand the low sulfur-tolerance of silver catalysts, in a later report [111], they calculated the adsorption energies of SO₂, SO₃, and SO₄ on the Ag/ γ -Al₂O₃. It was concluded that SO₂ irreversibly poisons the alumina support and single Ag-atom sites on the

alumina surface and that SO_2 can be potentially oxidized by NO_2 , resulting in poisoning the catalyst with SO_3 . But since regeneration was possible, surfaces of Ag nanoparticles were also suggested to play a role in this catalysis, and these – unlike the alumina support or atomically-dispersed Ag sites on alumina surface – can be regenerated. The step sites – Ag(211) – are amenable to regeneration because they catalyze the formation of HSO_x species that can easily desorb. Metal catalysts, in general, require co-feeding hydrogen to improve activity and facilitate regeneration. Future studies should aim at improving the activity and selectivity while reducing the loading of the noble metal.

Figure 7 A potential energy surface for the oxidation of NO over noble transition metals, Reprinted from *Applied Catalysis B: Environmental*, 113, Doronkin et al., “Study of the “Fast SCR”-like mechanism of H₂-assisted SCR of NO_x with NH₃ over Ag/Al₂O₃”, 228-236, Copyright (2012), with permission from ELSEVIER [110]

5. Discussion

Electronic structure theory, specifically density functional theory, has proven itself as an indispensable tool in modern catalysis research [112]. The current use of the theory has reached a level of sophistication that allows for extrapolating the atomic-scale understanding of the catalyst surface and reactive events at the elementary step level to experimentally measurable quantities such as turnover frequency, selectivity, and reaction orders through detailed microkinetic

modeling. We have discussed the contribution of computational methods in heterogeneous catalysis through three illustrative examples; similar examples abound in transition metals for: steam reforming [113-116], water-gas shift [117-122], methanol synthesis [123-128], Fischer-Tropsch synthesis [129,130], and alkane hydrogenolysis [131,132] among others. The strong interaction between theory and experiments, so much encouraged by Haldor Topsøe, and shown to be pivotal in realizing the advances referred to in these three examples discussed in detail above, is also a key to elucidating reaction mechanisms and to identifying potentially improved catalytic sites for a variety of heterogeneously catalyzed reactions.

One approach in the context of rational catalyst design has been to identify catalytic descriptors that can, in turn, be used to probe activity and selectivity trends across a family of catalysts by constructing volcano plots. In the context of transition metal catalysts, a combination of binding energy descriptors, linear scaling relations [7,15] and BEP correlations [8,133] have been used to construct such volcano plots [12,15,16,18,48,82,83]. For other catalytic materials, different descriptors have been proposed such as the metal-sulfur bond energy for transition metal sulfides [81] and NH_3 adsorption energy on zeotype catalysts [134]. Microkinetic modeling [135] allows for taking advantage of the continuum space of reactivity descriptors generated by these linear correlations and for constructing the reactivity/selectivity volcanos referred to earlier.

Catalyst characterization techniques offer valuable information on the nature of the active sites to be used for the DFT modeling. Further, it is often the case that DFT parameters have to be adjusted to yield results that are comparable to kinetics experiments [12,136]. Careful analysis of the modifications to the DFT derived parameters (needed to match the experimentally measured quantities) provides valuable insights as to how different the hypothesized model where the original DFT work was done might be from the active site under reaction conditions. For

instance, if the required adjustments to DFT-derived values in the microkinetic model are larger than the range of accuracy of DFT (0.2-0.3 eV [137]), it is possible that the model surface used in DFT calculations is not representative of the actual active site of the catalyst, and other sites need to be explored, as has been demonstrated recently for formic acid decomposition on gold [138]. After identifying the active site for several simple (e.g.: monometallic) catalysts, one can then construct volcano plots, and use them as maps to identify improved catalysts. These novel catalyst candidates can be tested rigorously using DFT, prior to their synthesis and experimental kinetics studies. Hence, an integrated approach for rational catalyst design emerges, wherein theory guides [139] and benefits from experiments. A relevant example was provided recently by Nørskov and coworkers [123] who computationally discovered a Ni-Ga alloy catalyst promising for carbon dioxide conversion to methanol, which was subsequently synthesized and experimentally proved to deliver on its promise.

The accuracy of DFT predictions depend on several factors including the choice of exchange-correlation functional [6,140]. The quality of DFT results could be estimated from comparison to experiments or higher-level theories [141]. The errors in DFT predictions lead to an overall error in the prediction of the net reaction rate. Recently, however, Nørskov and coworkers [141] showed, using a Bayesian framework (BEEF-vdW exchange-correlation functional), that correlations between the errors in the calculated adsorption and transition state energies tend to reduce this overall error. In a similar vein, Nørskov et al. [136] showed that varying degrees of mixing between RBPE and PW91 functionals had small effect on the total rate of NH_3 synthesis. This was attributed to a compensating effect in which the dissociation barrier of N_2 and the stability of intermediates vary in such a way as to minimize the impact of the variation in the exchange correlation functional over the calculated rates. This compensation was most

pronounced near the tip of the volcano. It is, however, important to note that for less active catalysts, where the errors can be less correlated, qualitative trends in activity and selectivity could still be determined. Therefore, the practical value of DFT is its ability to qualitatively describe the trends among a family of related catalytic materials, and thereby point out promising candidates for further theoretical and experimental investigation.

Conclusion:

Haldor Topsøe has been, for several decades, instrumental in nurturing the synergy between theory and experiment in heterogeneous catalysis for the ultimate goal of developing new industrial technologies. The three areas discussed here represent prime examples whereby the advancement of fundamental scientific understanding of physical/chemical transformations at the atomic-scale has benefited industrially relevant processes greatly. Clearly, the resolution of numerous challenges facing current and future generations of catalysis experts must navigate the path established by Haldor Topsøe and his scientific associates. Successes outside that path would only be examples of serendipity.

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