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Review Article

Perspective—Concerning a New Mechanistic Model Toward the Catalytic Ammonia Synthesis

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Abstract

A reasonable catalytic mechanistic model should refer to a widely range of catalytic reaction. We believe that all types of catalytic reaction on heterogeneous catalysis should follow a general mechanism, and it is our opinion that with the hall-filled valence orbitals, the atom of catalysts could convert the reactant into reactive radical and/or support the formation of new chemical bond between two reactants via radical dimerization. In our recent publications this new mechanistic model on the catalytic Fischer-Tropsch reaction (the conversion of CO and H_2 to hydrocarbons), electrochemical hydrogen evolution reactions, and hydrogen combustion in various metal catalysts is discussed, and which seems to provide a reasonable interpretation to those catalytic reactions. In the present work it is discussed that this new mechanistic model is suitable to the Haber-Bosch process (catalytic ammonia synthesis) on various transition metal catalysts, and a reasonable explanation is provided on the catalytic property of various transition metal for ammonia synthesis.

Keywords

Ammonia Synthesis, Catalytic mechanism, Haber-Bosch Process, Radical Center, Mechanistic Model

1. Introduction

Mechanism research in catalytic chemistry is both fascinating and confusing, particularly when it comes to solid-state catalysts, the nature of catalytic behaviours has been unidentified so far. The selection of active catalysts for the synthesis of product in industry has always been through the hit-and-trial method. This involves many failed attempts resulting in a waste of resources and energy. For example, the classic iron-based catalysts for ammonia synthesis were discovered via testing more than 2500 different catalysts in 6500 experiments by Mittasch and co-workers [1, 2]. Therefore, to save the time and cost involved in the development of an efficient and promising catalyst, a proper understanding of the reasonable mechanism involved in the catalytic activity is a basic requirement.

In our recent publications it is assumed that the metal atom with unpaired electrons on valence orbitals is a radical centre with one or more unpaired electrons (half-filled orbitals), which can convert spin-paired reactant into reactive radical state by radical abstraction or addition starting the chemical reaction or can adsorb two reactants by radical dimerization supporting the formation of new chemical bond as shown in Figure 1. This assumption can provide an illuminating explanation to the catalytic property of various catalytic reactions, such as copper metal for conversion CO_2 into a widely

range of products [3], various transition metals for electrochemical hydrogen evolution reaction [4, 5], H_2 oxidation into H_2O with addition of copper powder, and Fischer-Tropsch reaction on various transition metals [6]. In the present work we wish to continually show the line of thought in catalytic ammonia synthesis, hoping that this approach may be useful to some researchers in area of catalytic chemistry.
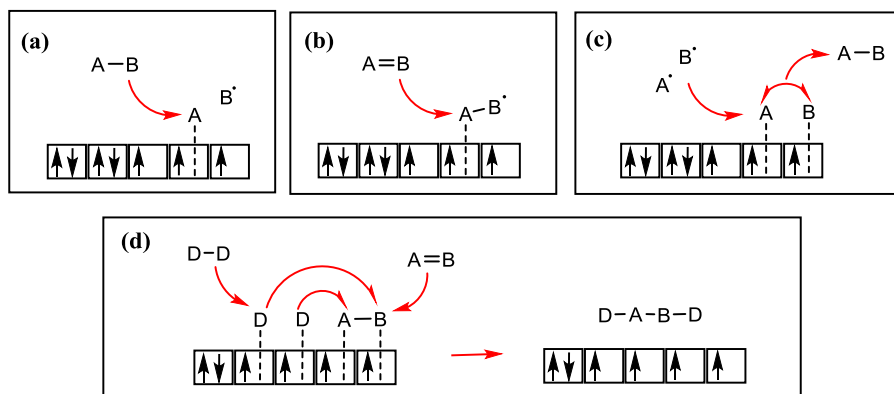

Figure 1. The process of catalytic reaction on metal atom with unpaired electrons: (a) a spin-paired reactant (A-B) is converted into free radical (B•) and bonded species via radical abstraction; (b) a spin-paired reactant (A=B) with double bond is converted into adsorbed radical via radical addition; (c) two active radicals (A• and B•) are bonded on the atom of metal surface via radical dimerization to support the formation of new chemical bond (A-B bond); (d) two spin-paired reactants (D-D and A=B) are bonded on the atom of metal surface via radical addition to support the formation of new chemical bond (D-A and B-D bonds).

2. Analysis of the Reported Results on Various Transition Metal for Catalytic Ammonia Synthesis

To understand the catalytic behaviour of some popular metals which have been used as a catalyst for the synthesis of ammonia, a comparison of the electronic configuration of various metal atom is given. Based on previous literature reports, the catalytic activity of iron ([Ar] $3d^6 4s^2$), cobalt ([Ar] $3d^7 4s^2$) and nickel ([Ar] $3d^8 4s^2$) is in the order Fe > Co > Ni as shown in Figure 2 [2]. Those three metals lie in the same period in the periodic table which means most of the properties are similar. The major difference is the number of half-filled valence sub-orbitals (HFO); Iron has four HFOs on the 3d-orbital, Cobalt has three HFOs on 3d-orbital and Nickel has two HFOs on the 3d-orbital. In other words, Fe has four unpaired electrons with a potential to facilitate the catalytic behaviour whereas, Co and Ni have only three and two respectively, so it may reduce the catalytic ability of these two metals as compared to iron. Likewise, the metal Ruthenium ([Kr] $4d^7 5s^1$) and Osmium ([Xe] $4f^{14} 5d^6 6s^2$) showed active and efficient activity for catalytic ammonia synthesis in experiments as well [2]. By looking at the configuration of electrons on these elements, it can be noticed that there is a similar valence electronic configuration as that of Iron; four HFOs. This supports the concept that the number of accessible HFOs is the major factor behind the catalytic activity of the catalysts. As a result, identical to our previous publication on the catalytic property of various metals for hydrogen evolution and Fischer-Tropsch reaction [4, 6], knowing the relationships between these HFOs on the atom of metal catalysts and the reactant species (H_2 and N_2) is critical for completely understanding the catalytic process.
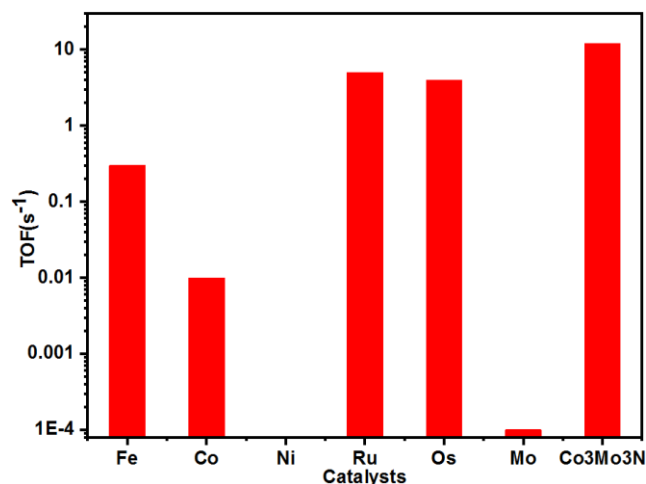
Figure 2. Calculated turnover frequencies for ammonia synthesis. All of the dates were from previously reported experimental result (Jacobsen et al., 2001). Under the same reaction conditions. The iron metal catalyst has better catalytic activity than cobalt, while the nickel and molybdenum catalysts have the lowest performance. Metals Ru and Os have similar catalytic activity, which is superior to iron metal. but the Co$_3$Mo$_3$N catalyst is found to be the best for catalytic ammonia production.

In the present paper, based on the above discussion on the catalytic behaviour of various catalysts for the ammonia synthesis, we assumed that the surface atom of metal (Fe, Co and Ni) is a radical centre with multiple unpaired electrons, which can bond hydrogen and nitrogen molecule via radical abstraction and addition and support the formation of H-N bonds on the outermost iso-surface on metal atom during the catalytic reaction process. Based on this assumption, it seems to be that the mechanism of catalytic activity of various metal catalysts in the synthesis of ammonia can be clearly described.

3. Discussion of the Process of Ammonia Synthesis on Various Transition Metal Surface

Firstly, the process of iron-catalysed ammonia synthesis is used as an example to demonstrate the process of catalytic reaction. As shown in Figure 3a, four accessible HFOs on the 3d-orbital of the iron atom. Step 1: two HFOs of an iron atom interacts with one covalent bond on a N_2 molecule via radical addition, while the remaining two HFOs on this iron atom link with two atomic H via radical abstractions or dimerization (Part I). Then, two bonded atomic H interact with bonded N=N specie forming two N-H bonds on two nitrogen atoms and releasing HFOs for further interaction (Part II). Step 2: Two more atomic H and left N=N bond on HN=NH species interact with released HFOs on iron and repeat Step 1, the formed bonded H and HN-NH specie interact to form two more N-H bonds. Step 3: Finally, two more H atoms and the last N-N bond on HN-NH specie interact with HFOs on iron and two NH_3 molecules formed after interaction of bonded atomic H and NH_2 species. As a result, the formation of two NH_3 molecules on an iron active atom requires three hydrogen transfer steps in total. Since Ru and Os have been experimentally proven to be active toward ammonia synthesis and have four accessible HFOs on their atom as well, it can be assumed that they follow the same catalytic reaction process for ammonia synthesis. Here, we shall not show more.

There is also a reasonable explanation for the reduced catalytic reaction rate found on cobalt catalyst compared to iron catalysts. This is due to only three accessible HFOs on a cobalt atom, there is just one HFO available for interaction with a hydrogen to form boned atomic hydrogen after a nitrogen molecule interacts with two HFOs to generate bonded N=N, HN-NH or NH_2 species on a cobalt active site (Figure 3b). This means that since just one hydrogen atom is transferred to a nitrogen atom to establish one N-H bond every time, it takes six hydrogen transfer steps to generate two NH_3 molecules on an effective cobalt site. This is twice as many steps as with iron catalyst, which require just three hydrogen transfer steps to make two NH_3 molecules. As a result, the reaction rate and catalytic activity on cobalt catalysts for catalytic ammonia synthesis are lowered.

There are only two HFOs accessible in the case of nickel.

No HFOs remain for bonding atomic hydrogen on an active Ni atom after interaction with a nitrogen molecule to generate bonded N=N specie, or no HFOs remain for the nitrogen molecule when bonded atomic hydrogen developed (Figure 3c). This indicated that there is no iso-surface given for simultaneously forming bonded atomic hydrogen and nitrogen molecule on a Ni atom. As a result, when Nickel was utilized as the catalyst for ammonia production, no activity was detected experimentally.

Furthermore, as with ordinary covalent bonds, electronegativity (EN) has a large impact on the ability of bonding atomic hydrogen or nitrogen molecules on the surface of metal atom. Although Fe, Ru, and Os metals have identical amount of accessible HFOs on their valence layer, there is a variance in catalytic activity when utilised as ammonia synthesis catalysts. Ru and Os outperform Fe catalysts [2] due to iron's weaker electronegativity (2.32) compared to Ru (2.65) and Os (2.72) [7]. lower EN makes the ability of bonding atomic hydrogen on Fe is somewhat weak, resulting in lower activity for driving ammonia synthesis in contrast to Ru and Os metals.

According to the findings of this analysis, the overall rate of reaction for ammonia synthesis will be effectively boosted if a sufficient number of HFOs are accessible on the surface-active site of the catalyst for interaction with the reactant species. Molybdenum ([Kr] $4d^5$ $5s^1$) contains a total of six HFOs (five on 4d-orbital and one on 5s-orbital). However, molybdenum exhibiting lower EN has a greater reaction affinity for nitrogen gas, it can combine directly with N_2 to yield a stable covalent Mo_2N product [8]. Consequently, the Mo loses its partial HFOs. This might explain why Mo metal catalyst for ammonia synthesis perform poorly (Figure 2). However, this problem could be overcome by combining molybdenum with suitable other elements, which exhibit a high electronegativity and change the electronegativity of Mo atom. In this condition, the molybdenum atoms would lose its strong attraction for nitrogen gas and instead function as a catalyst for ammonia synthesis. One such example is forming Mo_6N-octahedra as shown in Figure 3d, which can co-exist in the η-carbide crystal structure with Co, Fe or Ni to form Co_3Mo_3N, Fe_3Mo_3N or Ni_2Mo_3N, respectively [9-11]. In these compounds, there is only one strong Mo-N bond on each Mo atom and one nitrogen bond three Mo atoms via three strong covalent bonds. but the bonds between metal atoms are similar in metal crystal. Therefore, it can be expected that only one-sixth of HFO on Mo atom is occupied by nitrogen via strong covalent bond, five-sixths of HFOs are available for interaction in those compounds compared to Mo_2N (three-fourths). This unique chemical can demonstrate a respectable catalytic behaviour in the production of ammonia and have been observed from experiment (Figure 2) [2]. It should be pointed out that Co_3Mo_3N have two active sites (Co sites and Mo sites). The catalytic ammonia synthesis on Co atom (with three accessible HFOs) still follows a six-step reaction pathway as shown in Figure 3b. However, catalytic

activity should be dominated by Mo-sites with five accessible HFOs, due to only two steps being required for formation of two NH_3 molecules as shown in Figure 3d. This also explains why Co_3Mo_3N has higher activity for ammonia synthesis than pure Fe, Ru, or Os catalysts [2], which have just four HFOs accessible and require three catalytic reaction steps to make two NH_3 molecules. In addition, a similar catalytic activity for ammonia synthesis was observed on Co_3Mo_3N, Fe_3Mo_3N and Ni_2Mo_3N compounds in experiments [12], further confirming that Mo sites on Mo_6N-octahedra in those compounds dominate the catalytic process. If cobalt sites dominate the catalytic activity, there should be a noticeable difference in catalytic activity and no activity should be observed on Ni_2Mo_3N. Experiments recently discovered that Mo_6N-octahedra also can coexist in a η-carbide crystal structure with platinum and palladium to generate Pd_2Mo_3N and Pt_2Mo_3N [10, 12-14], which, here, were anticipated to exhibit catalytic active behaviours in the synthesis of ammonia.
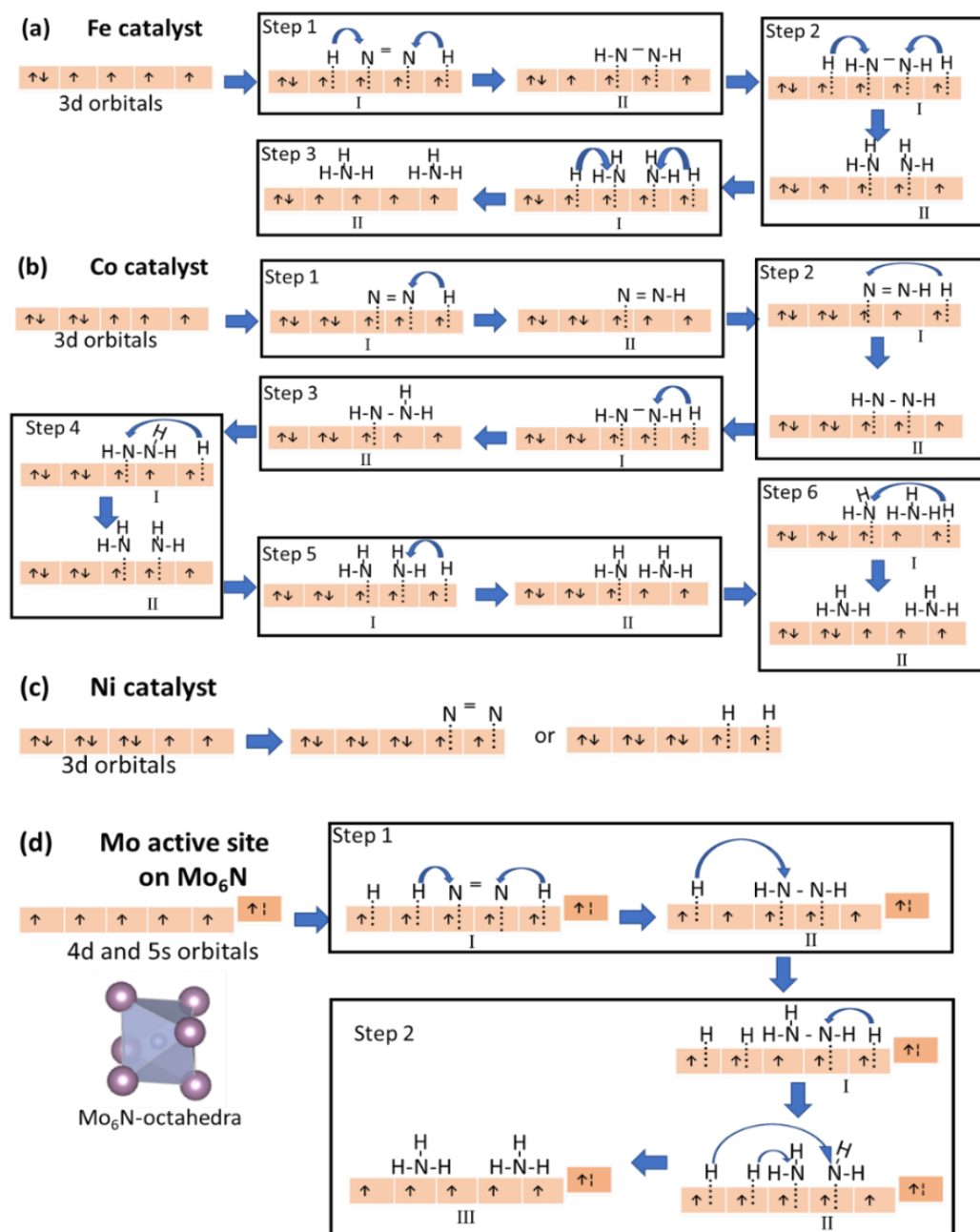
Figure 3. *Illustration of the process of catalytic ammonia synthesis on various catalysts' sites. The atoms situate on corner sites of crystal (a) iron catalyst with four HFOs exposed on active sites, three catalytic reaction steps are required for formation of two NH_3 molecules. (b) Three HFOs exposed on cobalt site, and six catalytic reaction steps are needed to form two NH_3 molecules. (c) only two HFOs exposed on the nickel site, no HFOs left for atomic hydrogen after interaction with nitrogen molecule, or no HFOs for nitrogen molecule when it interacts with atomic hydrogen. (d) After one HFO interact with a nitrogen atom, the Mo in Mo_6N-octahedra still has five HFOs lying on the atom's outermost iso-surface. As a consequence, forming two NH_3 molecules requires just two catalytic reaction steps.*

Based on our proposed catalytic reaction mechanism, an order of the catalytic activity on pure metals of the group of VII as catalysts for the synthesis of ammonia can be predicted given as; $Ru \approx Os > Fe > Ir \approx Rh > Co > Ni \approx Pt \approx Pd$. The elements of groups of VIB ($(n-1)d^5 ns^1$) and VIIB ($(n-1)d^5 ns^2$) have more accessible HFOs in metal. but low EN results in a loss of catalytic activity for ammonia synthesis. However, these elements have the potential to be compounded with elements from the VA or VIA groups, raising their electro-negativity, then following the same reaction scheme as in the case of Mo conversion to Mo_6N in compound of Co_3Mo_3N with efficient catalytic activity for the ammonia synthesis. Of course, it remains a key needed for sufficient HFOs to be accessible on the active site following the compound, ensuring that essential reactant species can interact with the catalytic active atom and boosting the catalytic reaction rate. There are no more than three HFOs accessible on the outermost of an atom in elements located on groups of IB ($(n-1)d^{10} ns^1$), and IIB ($(n-1)d^{10} ns^2$), making catalytic behaviour for ammonia synthesis impossible on these metal catalysts.

In solid-state catalyst research, higher surface areas have been shown to boost catalytic activity. Our assumption could account for this behaviour. As we have suggested in our previous publications [3-6], on the iso-surface of the atom, due to the orbital orientations in space, a part of the orbitals on the outermost of an atom might be blocked by neighbouring atoms in crystal and that those totally blocked sub-orbitals could not interact with HFOs on reactant forming bonded species during the catalytic process. However, when considering atoms on the surface, a portion of the valence sub-orbitals on a particular atom is still accessible with the portion of electron density available for surface interactions. an HFO with a part of its electron density exposed on the catalytic site can interact with HFO on reactant species, which then a bonded species forms. Based on the location of those atoms on the crystal structures, the ratio of valence sub-orbitals with the part region of electron density accessible is different. This variation depends on where those atoms are located on the crystal structure. When an atom is lying on the inner basal plane, one-third of sub-orbitals have part region of electron density exposed, two-thirds of sub-orbitals have a region of its electron density exposed when an atom is lying on the edge site, and all sub-orbitals have region exposed when an atom is situated on the corner of a crystal. The 3d-orbital has five sub-orbitals, each of which exposes a part of the electron density while the atoms are lying in the corner. Each atom on the edges has two sub-orbitals that reveal a part of the electron density region. Atoms on the centre of crystal have just one sub-orbital with a visible zone of electron density. This means that the atoms on the inner basal plane and edge sites of the iron crystal might display one or two HFOs, respectively. All four HFOs may be available when atoms lied on the corner sites, where they could interact with the required reactant species to form two bonded atomic H and one boned

N_2 molecule during catalytic ammonia production. This demonstrated that only corner iron atoms are active sites during the catalytic ammonia synthesis process, explaining why reduced iron on the nanoscale could achieve the catalytic activity to drive ammonia synthesis. As a result, the highest surface area is a fundamental prerequisite for building efficient solid-state catalysts to drive ammonia synthesis. As of now, all the developed ammonia catalysts are built on the highest exposed surface.

4. Conclusion

In this study, based on the comparison between catalytic behaviours for ammonia synthesis and electronic structure of atom of various catalysts, it is found that the sufficient active HFOs on an active atom, as an active catalyst for ammonia synthesis, are basic requirement. It is assumed that the surface atom of metal is radical centre with multiple unpaired electrons, which can interact with nitrogen molecule and atomic hydrogen via radical reaction simultaneously to support the formation of H-N bonds. This assumption is not only showing a decent explanation for reported experimental results, but also is the use of predicting the catalytic ability on various catalysts.

The process and the difference in catalytic behaviour on various catalysts of catalytic ammonia synthesis are successfully illustrated. In the view of these excellent agreements of our analysis with experimental results. We believe that it is also suitable for more other catalytic reaction process, and which will be discussed in our future publications.

Anyhow, it was observed from reported experimental results that certain correlation exists between accessible number of half-filled orbitals on catalytic atom and their catalytic behaviours in the course of catalytic ammonia synthesis. A correlation between them needs to be confirmed by further investigations.

Abbreviations

HFO   Half-Filled Valence Sub-Orbitals

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Author Contributions

Youyi Sun is the sole author. The author read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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Research Field

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