

CHAPTER I

INTRODUCTION

1.1 Background

The search for alternative energy sources, which are efficient, economic and friendly environmental becomes one of the most urgent tasks of our society. One of the renewable energy sources is hydrogen. Although, hydrogen energy has been known for a long time, only recently it is intensively explored due to the development of hydrogen-based fuel cell power source for the transportation sector. The molecular hydrogen needed as an on-board fuel for hydrogen vehicles can be obtained through many thermochemical methods utilizing natural gas, coal (by a process known as coal gasification), liquefied petroleum gas, biomass (biomass gasification), by a process called thermolysis. Hydrogen can also be produced from water by electrolysis or by chemical reduction using chemical hydrides or aluminium [1]. Environmental consequences of the production of hydrogen from fossil energy resources include the emission of greenhouse gases, a consequence that would also proceed from the on-board reforming of methanol into hydrogen. Studies comparing the environmental consequences of hydrogen production and use in fuel cell vehicles to the refining of petroleum and combustion in conventional automobile engines find a net reduction of ozone and greenhouse gases in favor of hydrogen. Hydrogen production using renewable energy resources would not create such emissions or, in the case of biomass, would create near-zero net emissions assuming new biomass is grown in place of that converted to hydrogen. The scale of renewable energy used today is insufficient and would need to be greatly increased to meet demand for widespread use in transportation. However, in a few countries, hydrogen is being produced using renewable sources.

In the past, research into hydrogen storage materials has intensified because of an increased interest in environmentally fuels. There was increasing interest in the development of hydrogen based fuel cells [2] as an environmentally friendly power source which is suitable for use in the transportation sector [3]. A critical issue with hydrogen as a fuel for use in transportation systems was the need for efficient

amine has been suggested as a potential candidate for hydrogen storage owing to its high hydrogen content and a source of hydrogen for use in motor vehicles as it can be made to release hydrogen on heating, being polymerized first to $(\text{NH}_2\text{BH}_2)_n$, and then to $(\text{NHBH})_n$. Borane amine finds some use in organic synthesis as an air-stable derivative of diborane.

1.3 Alane amine, borane phosphine and alane phosphine

Alane amine (AlH_3NH_3), borane phosphine (BH_3PH_3) and alane phosphine (AlH_3PH_3) are the chemical compounds of which the structure and charge distribution are very similar to the borane amine (BH_3NH_3). They are different derivatives of borane amine, which have recently been shown to be the promising materials for chemical hydrogen storage. Because of Al and B atoms in the periodic table are arranged in the same group (IIIA), N and P atoms in the periodic table are arranged in the same group (VA) that groups the elements according to their similar properties, therefore AlH_3NH_3 , BH_3PH_3 and AlH_3PH_3 may all be good systems for hydrogen storage. Our current interest is to search for other candidates for hydrogen storage systems to identify alternatives that may be easier to synthesize and for which we can design new catalysts. We have chosen to study the molecular systems, different derivatives of borane amine and those compounds containing B, Al, N, and P atoms.

1.4 Literature reviews

Extensive theoretical and experimental research investigated the properties and molecular mechanism for hydrogen release from borane amine and isovalent systems including alane amine, borane phosphine and alane phosphine. Many experimental and computational chemistry researches have also been shown to possess appropriate thermodynamic properties to serve as hydrogen storage systems.

In the 2002s, Baitalov *et al.* [11] investigated the thermally activated decomposition of borane amine, BH_3NH_3 in the temperature range up to 500 K using differential scanning calorimetry (DSC) and thermogravimetry (TG) combined with the FTIR spectroscopic and mass spectrometric analysis of the gas phase, which indicated that BH_3NH_3 undergoes stepwise thermal decomposition in the temperature range up to 500 K. They found that BH_3NH_3 is already decomposed at 410 K. The

exothermic decomposition is accompanied by the release of approximately 2.2 mol H₂/mol BH₃NH₃. This corresponds to a remarkable hydrogen storage density of 14.3 mass% related to the mass of borane amine. The other decomposition products are aminoborane (H₂BNH₂), polymeric aminoborane (H₂BNH₂)_x and a small amount of the volatile borazine (BHNH)₃, which is the boron–nitrogen analog of benzene, and traces of diborane (B₂H₆) were also found in this system.

In the 2005s, Li *et al.* [12] have theoretically studied the hydrogen abstraction reaction of H₃BNH₃ → H₂ + H₂BNH₂. The geometries of all the stationary points are optimized at the B3LYP and MP2 levels of theory with a series of basis sets up to aug-cc-pVTZ. The energies are refined using the G3, G3MP2, G3MP2B3, CBS-Q, CBS-Q//B3, and a combined high-level method based on the geometries optimized using the B3LYP/aug-cc-pVTZ level of theory. The rate constants are evaluated using the conventional transition-state theory and canonical variational transition-state theory (CVT). The rate constant calculated from the CVT/SCT method is $k(T) = 6.86 \times 10^6 \times T^{1.69} \times e^{(-1.37 \times 10^4/T)} \text{ s}^{-1}$. In the same year Grant *et al.* [6] studied thermodynamic properties of molecular borane phosphine, alane amine, alane phosphine and the [BH₄⁻][PH₄⁺], [AlH₄⁻][NH₄⁺], and [AlH₄⁻][PH₄⁺] salts using CCSD(T) at the aug-cc-pVTZ basis set. From calculation results, they found that alane amine (AlH₃NH₃) and the salts [AlH₄⁻][PH₄⁺] and [BH₄⁻][PH₄⁺] have the potential to serve as hydrogen storage systems. The hydride affinity of AlH₃ is calculated to be -70.4 kcal/mol at 298 K. The proton affinity of PH₃ is calculated to be 187.8 kcal/mol at 298 K in an excellent agreement with the experimental value of 188 kcal/mol.

In the 2006s, Xu and Chandra [4] have studied catalytic performance of supported non-noble metals, Co, Ni and Cu for hydrogen generation from aqueous BH₃NH₃ at room temperature. Support effects on the catalytic activity have been investigated by testing the hydrogen generation reaction in the presence of Co supported on γ-Al₂O₃, SiO₂ and C and it was found that the Co/C catalyst has higher activity, whereas the supported Fe is catalytically inactive for this reaction. Activation energy for hydrogen generation from aqueous BH₃NH₃ in the presence of Co/γ-Al₂O₃ was measured to be 62 kJ/mol. Furthermore, they have studied the particle size, surface morphology and surface area of the supported metal catalysts using the X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive X-ray

(EDX) and BET experiments. They found that with decreasing the particle size the activity of the supported catalyst is increased.

In the 2007s, Nguyen *et al.* [13] have theoretically studied molecular mechanism for hydrogen release from borane amine (BH_3NH_3) and ethane (C_2H_6), including the catalytic role of the lewis acid BH_3 using various methods, up to the coupled-cluster CCSD(T) level, in conjunction with the aug-cc-pVnZ basis sets with $n = \text{D, T, and Q}$, extrapolated to the complete basis set limit, show that the borane molecule (BH_3) and ammonia molecule (NH_3) behave as a Lewis acid catalyst in the hydrogen elimination reactions of XH_nYH_n systems ($\text{X, Y} = \text{C, B, N}$) but with less capability to reduce the barrier height. From calculated results, they found that the barrier height for hydrogen release from borane amine corresponds to a reduction of 30.4 kcal/mol and 13.0 kcal/mol with the presence of BH_3 and NH_3 , respectively. Moreover, they have analyzed the kinetic properties of these processes by both TST (transition state theory) and RRKM (Rice-Ramsperger-Kassel-Marcus theory).

In the same year, Xu and Chandra [7] studied the hydrogen release from catalytic hydrolysis reaction of borane amine at room temperature. They found that the noble metals on suitable supports significantly enhance the catalytic activities. The $\gamma\text{-Al}_2\text{O}_3$ supported Ru, Rh, and Pt catalysts are highly active for the hydrolysis of BH_3NH_3 , exhibiting hydrogen release of $\text{H}_2/\text{BH}_3\text{NH}_3 = 3.0$ in 3.0, 1.3 and 0.75 min, respectively. The $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst shows a lower catalytic activity, releasing hydrogen of $\text{H}_2/\text{BH}_3\text{NH}_3 = 2.9$ in 120 min. The $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ catalyst exhibits a much lower catalytic activity for hydrolysis of *aq.* BH_3NH_3 , releasing hydrogen of $\text{H}_2/\text{BH}_3\text{NH}_3 = 1.9$ in 610 min. In comparison, the $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts are lower than the $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$, $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalysts but higher than the $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

In the 2008s, Nguyen *et al.* [14] have theoretically studied electronic structure calculations at the CCSD(T) level with the aug-cc-pVnZ and aug-cc-pV(n+d)Z basis sets for hydrogen release from alane amine without and with the presence of alane (AlH_3). The calculated results demonstrate that alane can play role of an efficient bifunctional catalyst for hydrogen release from alane amine. The barrier height in the catalytic pathway for hydrogen release from alane amine with AlH_3 as the catalyst is 18.7 kcal/mol. Furthermore, comparison with the reaction pathways of hydrogen release from borane amine (BH_3NH_3) with AlH_3 or BH_3 as the catalyst shows that

AlH_3 is a better catalyst than BH_3 . They predicted kinetic rate constants for hydrogen release from alane amine in the presence of AlH_3 are $k(298 \text{ K}) = 2.6 \times 10^{-2} \text{ s}^{-1}$ and $k(400 \text{ K}) = 8.4 \times 10^1 \text{ s}^{-1}$, including tunneling corrections.

1.5 Objective

In this study, the molecular mechanism and thermodynamic properties of hydrogen release from borane amine, alane amine, borane phosphine and alane phosphine have been theoretically studied using ab initio. The geometry, energetic, transition state structure and thermodynamic properties calculations using the B3LYP functional and second-order perturbation theory (MP2) with the 6-311++G(d,p) basis set have been used to predict the molecular mechanism of hydrogen release from borane amine, alane amine, borane phosphine and alane phosphine in systems with and without the borane, ammonia, alane and phosphine.