Catalytic performance of Ru, Os, and Rh nanoparticles for ammonia synthesis: A density functional theory analysis

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ABSTRACT

NH$_3$ synthesis on Ru, Os, and Rh nanoparticle catalysts was investigated using density functional theory calculations. The Ru and Os nanoparticles exhibited similar shapes, while that of Rh differed significantly. For all metal species, step sites appeared at nanoparticle diameters (d) >2–4 nm. The calculated activation barriers (E_a) were small at step sites, and Ru and Os step sites exhibited similar E_a values despite the former having a higher turnover frequency. This is likely due to the surface coverage of vacant sites being higher on Ru. Although the increase in NH$_3$ synthesis rate at d = 2–4 nm was common to Ru, Os, and Rh, the reaction rates decreased in the order: Ru > Os > Rh. Our results show that E_a values, surface vacant sites, and the number of step sites are important factors for NH$_3$ synthesis. The Ru nanoparticles exhibited high activity due to satisfying all three factors.

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1. Introduction

NH$_3$ (ammonia) synthesis is an area of particular importance in heterogeneous catalytic chemistry due to the use of NH$_3$ in a range of applications, including fertilizers and explosives. Thus, the catalytic synthesis of NH$_3$ was established in the early 20th century in the form of the Haber-Bosch process, which normally employs doubly-promoted iron catalysts [1,2] to generate NH$_3$ from N$_2$ and H$_2$ gases under a high pressure and temperature. Thus, to reduce the reaction temperature and pressure, the search for superior catalysts has received growing attention, with Ru being reported to be an excellent catalyst for this process [3–6].

However, to further improve catalyst performance, detailed information is required regarding the reaction energetics, as these factors are strongly related to the catalytic performance. For example, a Ru catalyst system is advantageous over Fe as NH$_3$ poisoning is less pronounced in the former. However, the Ru system is vulnerable to hydrogen poisoning [7–9], due to the presence of strong metal-hydrogen (M-H) interactions, thereby indicating that M-H interactions can significantly affect the catalytic performance.

Based on extensive theoretical research into the NH$_3$ synthesis [10–13] the key reactions involved in N$_2$ dissociation and NH$_x$ (x = 1–3) formation were found to be as follows:

$$N_2 + 2^* \rightleftharpoons 2N^* \tag{1}$$

$$H_2 + 2^* \rightleftharpoons 2H^* \tag{2}$$

$$N^* + H^* \rightleftharpoons NH^* + ^* \tag{3}$$

$$NH^* + H^* \rightleftharpoons NH_2^* + ^* \tag{4}$$

$$NH_2^* + H^* \rightleftharpoons NH_3^* + ^* \tag{5}$$

$$NH_3^* \rightleftharpoons NH_3 + ^* \tag{6}$$

where asterisk (*) denote the vacant adsorption site and species with asterisk is adsorbed ones. In addition, experimental and theoretical studies have identified that for a Ru catalyst, the rate determining step (RDS) is N$_2$ dissociation (Eq. (1)), a process that depends significantly on the catalyst surface structure [14,15]. For example, the activation energy of N$_2$ dissociation on Ru was shown to increase considerably when its step sites are inactivated [15]. In

the same study, theoretical computations indicated that these sites decrease the activation barrier of N_2 dissociation and thus significantly promote this reaction step. In addition, the importance of the surface structure for predicting the catalytic performance in the synthesis of NH_3 was further demonstrated by Honkala et al. who found that the presence of active sites (i.e., B_5 sites) for N_2 dissociation depends on the particle size [16].

To better understand the superior catalytic performance of Ru catalysts, comparison between different transition metal species is valuable, as it provides key information for the future development of high-performance catalysts. Such a comparison is often achieved using a volcano plot, which describes the thermodynamic tendency of M-N formation [17]. While this plot is sufficient for qualitative purposes, more detailed descriptions of the M-H or M-NH_x interactions are required for quantitative predictions. Thus, although detailed theoretical studies of NH_3 synthesis over other metal catalysts can provide useful information, few reports have been published to date. However, one important example originates from Song et al. who theoretically compared the N_2 dissociation and N-H formation processes on Pd, Zr, and Ru surfaces [18]. Their results indicated that the high activity of Ru is due to the balance between M-N and M-H interactions, where weak M-N interactions on Pd result in slow N_2 dissociation, and strong M-N interactions on Zr lead to a slow NH_x formation rate. The Ru catalyst therefore exhibited a superior performance due to the following key characteristics: (i) the moderate strength of the M-N interactions, since weak interactions are not sufficient to dissociate the N−N bond, and strong interactions lead to surface N poisoning, and (ii) the presence of a stepped surface, since the N_2 dissociation is more active than on a close-packed surface. These factors should be considered when carrying out a realistic prediction of NH_3 synthesis.

Although studies into single crystal surfaces could provide fundamental information, real catalysts often consist of nanosized metal particles of various shapes and sizes, which are highly dependent on the metal species itself. As such, a realistic prediction of catalytic performance over various metal systems should consider the surface structures of the nanoparticles.

Thus, we herein report our study into predicting the shape and morphology of metal nanoparticles based on a theoretical approach, followed by prediction of the system kinetics on the exposed facets, with the ultimate aim of gaining an insight into NH_3 formation. After a discussion regarding the theoretical background and computational details, we present the results of surface energy calculations and nanoparticle formation. Finally, the NH_3 formation reactions taking place on the surfaces of the various metal species are presented along with their corresponding catalytic performances.

2. Theoretical background and computational details

To predict the NH_3 synthesis activity over various metal species, it is essential to first determine which metal surfaces are exposed on the nanoparticles. Thus, theoretical predictions of the metal particle shapes have been carried out by approaches such as force field molecular dynamics and Monte Carlo simulations [19–22]. Among these approaches, the Wulff construction is frequently employed to understand and predict equilibrium shapes. Although this theorem is based on thermodynamics and describes macroscopic crystals, it is also applicable to sufficiently large nanosized crystals with diameters (d) >1.5 nm [23]. Indeed, a number of experimental studies using transmission electron spectroscopy (TEM) and high-resolution scanning transmission electron microscopy (HR-TEM) confirmed that the Wulff con-

struction gives the correct shapes for nanosized particles [24,25]. Recently, the combination of the Wulff construction with density functional theory (DFT) energetics has been applied to various systems [26–29], with satisfactory results in predicting nanoparticle shapes and explaining experimental observations [30–34].

The equilibrium form of crystals can also be predicted from Wulff's theorem, which can be derived by minimizing the Gibbs energy of the whole crystal surface. According to this theorem, the facet i of a metal particle should satisfy the following relationship:

$$\frac{h_i}{\gamma_i} = \text{constant} \tag{7}$$

where h_i is the normal distance of the surface i from the center of the particle, and γ_i is the surface energy of i. In the present study, the γ_i value of each facet was estimated from DFT calculations, and the surface energy was estimated by the following formula:

$$\gamma = \frac{1}{2A}(E_{\text{surf}}^{\text{tot}} - nE_{\text{bulk}}^{\text{tot}}) \tag{8}$$

where $E_{\text{surf}}^{\text{tot}}$ and $E_{\text{bulk}}^{\text{tot}}$ are the total energies per atom in the surface and bulk systems, respectively, while n is the number of metal atoms, and A is the surface area of the unit cell.

The kinetics of NH_3 synthesis on each metal facet were then analyzed. Initially, we estimated the reaction rate from the reaction energy (ΔE) and the activation energy (E_a), as determined by DFT calculations. For the reaction rate of NH_3 synthesis, the pseudo-steady state approximation was applied by taking the N_2 dissociation reaction as the single RDS. Under these conditions, the overall NH_3 synthesis reaction can be represented as follows:

$$R = r_1 = k_1 P_{N_2} \theta_*^2 \left(1 - \frac{1}{K_{\text{eq}}} \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}\right) \tag{9}$$

where θ_* is the coverage of surface vacant sites, and K_{eq} is the equilibrium constant of the whole reaction. In this case, θ_* can be evaluated as:

$$\theta_* = \left(1 + \sqrt{K_2 P_{H_2}} + \frac{P_{NH_3}}{\sqrt{K_2 P_{H_2}} K_5 K_6} + \frac{P_{NH_3}}{K_2 P_{H_2} K_4 K_5 K_6} \right. $$
$$\left. + \frac{P_{NH_3}}{(K_2 P_{H_2})^{3/2} K_3 K_4 K_5 K_6} + \frac{P_{NH_3}}{K_6}\right)^{-1} \tag{10}$$

where k and K indicate the rate constant and the equilibrium constant, respectively, and the subscript i corresponds to the i-th elementary step. Surface coverages of H, N, NH, NH_2, and NH_3 were calculated as follows:

$$\theta_H = \sqrt{K_2 p_{H_2}}\, \theta_*$$

$$\theta_N = \frac{p_{NH_3}}{K_2^{3/2} p_{H_2}^{3/2} K_3 K_4 K_5 K_6} \theta_*$$

$$\theta_{NH} = \frac{p_{NH_3}}{K_2 p_{H_2} K_4 K_5 K_6} \theta_* \tag{11}$$

$$\theta_{NH_2} = \frac{p_{NH_3}}{\sqrt{K_2 p_{H_2}} K_5 K_6} \theta_*$$

$$\theta_{NH_3} = \frac{p_{NH_3}}{K_6} \theta_*.$$

The reaction rate constant k_1 is estimated by the following formula that assumes the transition state theory [35]:

$$k_1 = \frac{k_B T}{h} \frac{q_{TS}}{q_{\text{gas}}} \exp\left(-\frac{E_a}{k_B T}\right) \tag{12}$$