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Theoretical design of nanocatalysts based on (Fe₂O₃)_n clusters for hydrogen production from ammonia

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18 ABSTRACT

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¹⁹ The catalytic activities of high-spin small Fe(III) oxides have been investigated for efficient hydrogen production through ammonia decom-²⁰ position, using the artificial force induced reaction method within the framework of density functional theory with the B3LYP hybrid ²¹ exchange-correlation functional. Our results reveal that the adsorption free energy of NH₃ on $(Fe_2O_3)_n$ (n = 1-4) decreases with increas-

- ²² ing cluster size up to n = 3, followed by a slight increase at n = 4. The strongest NH₃ adsorption energy, 28.55 kcal/mol, was found for ²³ Ee₂O₂ where NH₂ interacts with a two-coordinated Fe site forming an Fe₂N bond with a length of 2.11 Å. A comparative analysis of NH₂
- Fe_2O_3 , where NH₃ interacts with a two-coordinated Fe site, forming an Fe–N bond with a length of 2.11 Å. A comparative analysis of NH₃ dehydrogenation and H₂ formation on various Fe(III) oxide sizes identifies the rate-determining steps for each reaction. We found that the
- rate-determining step for the full NH₃ dehydrogenation on $(Fe_2O_3)_n$ (n = 1-4) is size-dependent, with the NH^{*} \rightarrow N^{*} + H^{*} reaction acting
- as the limiting step for n = 1-3. In addition, our findings indicate that H₂ formation is favored following the partial decomposition of NH₃ on Fe(III) oxides.
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³⁰ I. INTRODUCTION

■Q13 31

The ammonia decomposition reaction has recently received 32 extensive attention due to its potential use as an alternative green energy source.¹⁻⁵ This reaction typically requires a catalyst and 33 34 consists of two major steps. The first is ammonia dehydrogena-35 tion on the catalytic surface, leading to the formation of adsorbed nitrogen and hydrogen species. This is followed by nitrogen cou-36 pling, resulting in the formation of molecular nitrogen.⁶ One of the 37 key advantages of ammonia as a green energy source is its ability 38 39 to be liquefied at low pressures and a relatively low temperature 40 of 20 °C, making it an attractive candidate for hydrogen storage and transportation. As with many other chemical processes, catalysts play a crucial role in ammonia decomposition to achieve fast and efficient H_2 production. Experimental and theoretical studies have demonstrated that Ru-based catalysts are the most active for ammonia decomposition.^{6–8} However, ruthenium's high cost and limited availability pose challenges for its large-scale industrial application. Therefore, developing new types of cost-effective catalysts for NH₃ decomposition, based on non-noble metals or metal oxides, has become a significant area of research for effective hydrogen generation.⁹ Numerous studies have focused on the activity of catalysts involving various metals and alloys.¹⁰ Among the most studied non-noble metals, iron (Fe) stands out as a leading catalyst

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due to its low cost and availability. While the reactivity of Fe is 53 54 lower compared to other transition metals, it can be enhanced 55 by using nanoparticles instead of extended surfaces. Indeed, it is 56 well known that the reactivity of small-size clusters can be finely tuned by adjusting their size, geometry, and electronic structure, 57 58 making them promising catalysts in various catalytic processes.^{11–15} 59 For example, Nishimaki et al.¹⁶ experimentally studied ammonia 60 decomposition on Fe nanoparticles of various grain sizes (20 nm-1 61 μ m) in an ammonia steam environment. Their findings indicated 62 that the highly reactive surface of nanoparticles enhances NH₃ 63 dissociation without increasing the nitrogen content in the gas 64 phase, resulting in nitride phases that depend on the grain size and 65 morphology.

As an alternative approach, ammonia decomposition reactions 66 67 on small nanosized Fe clusters are frequently investigated using den-68 sity functional theory (DFT) methods. Theoretical studies suggest 69 that the mechanisms of ammonia decomposition involve stepwise 70 dehydrogenation, where the rate-limiting step can vary depending 71 on the size, type, and shape of the catalysts. Thus, Lanzani and 72 Laasonen employed spin-polarized DFT to examine the adsorption and dissociation of NH3 on a single nanosized icosahedral 73 74 Fe55 cluster.¹⁷ Their research indicated that the overall reaction 75 barrier for stepwise dehydrogenation was 1.48 eV, with different 76 active sites on the Fe55 cluster (facets and vertices), where the 77 rate-limiting step was the initial hydrogen dissociation. Similarly, 78 Otero et al.¹⁸ conducted a comprehensive comparative study on 79 various sizes of Fe clusters (Fe16, Fe22, Fe32, Fe59, Fe80, Fe113, and 80 Fe190) and Fe(111) surfaces with additional adatoms. Their find-81 ings indicated that the reaction kinetics were influenced more by 82 the strength of NH₃ adsorption rather than the activation energy 83 barrier. Stronger NH3 adsorption led to enhanced dissociation com-84 pared to desorption. The studies mentioned above primarily focus 85 on the catalytic activities of large Fe clusters and Fe surfaces in the ammonia decomposition reaction. However, Zhang et al.¹⁵ specifically investigated the activities of relatively small Fe clusters, ranging from single Fe atoms to Fe4 clusters. They found that the highest catalytic activity for stepwise NH₃ dehydrogenation was observed with nonatomic iron clusters. Interestingly, they observed that the rate-limiting steps differed: co-absorbate NH dissociation for Fe and Fe3 and co-absorbate NH2 dissociation for Fe2 and Fe₄.

The NH₃ decomposition reaction can be enhanced in the presence of oxygen, where it can proceed through various pathways, including ammonia oxidation and hydrogen evolution reactions. Moreover, metal oxides are commonly employed as catalyst supports in ammonia decomposition to enhance dispersion and catalytic stability. Among these supports, widely used materials include Al₂O₃, TiO₂, as well as carbon nanotubes and nanofibers.² However, metal oxides not only serve as supports but also play a crucial role in hydrogen evolution reactions in electrocatalysis, where the oxidation state of metals significantly influences the catalytic activity of ammonia decomposition. In particular, iron-based oxides, such as Fe₂O₃, are extensively studied forms of iron oxide due to their low cost and abundance, although their activity and stability can vary depending on their structure and size.

In this work, we elucidate the role of the size and structural effects on the catalytic activity of iron-oxide-based nano-catalysts

toward the efficient ammonia dehydrogenation process, which is the first step in the full ammonia decomposition reaction. In particular, we investigated the theoretical mechanisms of stepwise ammonia dehydrogenation on $(Fe_2O_3)_n$ clusters with n = 1-4 to compare the reactivity of different-sized Fe(III) oxides using the Artificial Force Induced Reaction (AFIR) method.^{32,33} In addition, we examined the NH₃ adsorption and various energy barriers for NH₃ dehydrogenation on different active sites of Fe(III) oxides. Our investigation aims to contribute to the design of nanocatalysts based on Fe₂O₃ by exploring the activity of small-sized Fe(III) oxide clusters.

II. COMPUTATIONAL DETAILS

All calculations were performed using spin-unrestricted Kohn-Sham DFT with Becke's three-parameter hybrid functional combined with the Lee, Yang, and Parr correlation functional, denoted as B3LYP.³⁴⁻³⁶ In our calculations, we have employed the LANL2DZ³ basis set with effective core potentials (ECPs), as well as the Pople-style $6-31+G^*$ basis set, equivalent to 6-31+G(d), which includes polarization (d) and diffuse (sp) functions, as it is implemented in the Gaussian 16 program.⁴⁰ These methods have been successfully applied to metals and metal oxide systems in previous studies. Thus, Glukhovtsev et al.41 reported that the performance of the B3LYP/ECP method for systems containing iron with various types of bonding showed good agreement with the experimental data and high-level theoretical methods {coupled-cluster 035 single double triple [CCSD(T)], MCPE, and complete active space 036 self-consistent field (CASSCF)}. Similarly, Taguchi et al.⁴² studied $Fe_6O_2(NO_3)_4(hmp)_8(H_2O)_{22}$, $[Fe_4(N_3)_6(hmp)_6]$, and $Fe_8O_3(OMe)$ (pdm)₄(pdmH)₄(MeOH)₂₅ clusters using the B3LYP/LANL2DZ level of theory, obtaining results that were consistent with the experimental data.

At the initial stage, the most stable isomers of iron trioxide for each selected size were investigated using the DFT method. A single iron trioxide molecule contains two Fe³⁺ ions; therefore, there are often several energetically accessible spin states (0, 1, 2, 3, 4, 5). For the starting cluster Fe_2O_3 , the lowest energy structure corresponds to the nonet state with a total spin S = 4. For $(Fe_2O_3)_2$, the lowest energy solution was found with a total spin S = 10, indicating an increase in the number of Fe³⁺ ions, which raises the total spin projection. For (Fe₂O₃)₃, the lowest energy structure was found with a total spin S = 15, and finally, in the case of $(Fe_2O_3)_4$, the lowest energy structure had a total spin S = 20. Therefore, all clusters considered in our study were in a ferromagnetic configuration. We confirmed that spin contamination in the low-lying energy structures was negligible and conducted wavefunction stability analysis for all configurations to ensure the absence of instability.

To analyze the most favorable pathways of NH₃ dehydrogenation and H₂ formation reactions catalyzed by small $(Fe_2O_3)_n$ (n = 1-4) clusters, we applied the SC-AFIR and DS-AFIR methods implemented in the Global Reaction Route Mapping (GRRM) strategy.^{32,43–46} These automated reaction path search methods have been successfully applied to many catalytic reactions in combination with DFT methods.^{33,47-50} The basic idea in the AFIR strategy is to push fragments (reactants) A and B of the whole system together or pull them apart by minimizing the following AFIR function:³²

ARTICLE

$$F(Q) = E$$

$$F(Q) = E(Q) + \alpha \frac{\sum_{i \in A} \sum_{i \in B} \omega_{ij} r_{ij}}{\sum_{i \in A} \sum_{i \in B} \omega_{ij}}.$$
 (1)

169 The external force term in (1) perturbs the given adiabatic 170 Potential Energy Surface (PES), E(Q), with geometrical parameters 171 Q in the AFIR function. Here, α defines the strength of the arti-172 ficial force, which depends on the weighted sum of the inter-173 atomic distances r_{ii} between atoms i and j, with the weights ω_{ii} defined as 174

$$\omega_{ij} = \left[\frac{R_i + R_j}{r_{ij}}\right]^6,$$
 (2)

177 where R_i and R_j are the covalent radii of atoms *i* and *j*, respectively. 178 The force parameter α in (1) can be expressed as follows:

$$\alpha = \frac{\gamma}{\left[2^{-1/6} - (1 + \sqrt{1 + \gamma/\varepsilon})^{-1/6}\right]R_0},$$
(3)

180 where R_0 and ε are the parameters corresponding to interatomic Lennard-Jones potentials and the parameter y has a physical 181 meaning of a collision energy. 182

183 This perturbation of the PES facilitates the exploration of addi-184 tional approximate transition states (TS) and local minima on the 185 surface. The model collision energy parameter γ in (3) serves as 186 an approximate upper limit for the barrier height that the system 187 can be affected by the AFIR function.³² In our calculations, γ was 188 set to 300 kJ/mol for the entire system. During the initial reaction 189 path search, the LANL2DZ basis set was applied with an artifi-190 cial force to yield approximate products and transition states (TS). Subsequently, we utilized the $6-31+G^*$ basis set to optimize these approximate transition states and local minima without the artificial force, employing the Locally Updated Plane (LUP) method. The vibrational frequency calculations have been performed to confirm the nature of the stationary points, whether they are minima or transition states. The results presented in this paper include reaction route mapping at the B3LYP/LANL2DZ level and reaction pathways at the B3LYP/6-31+G(d) level.

The binding energy E_b per unit *n* of a $(Fe_2O_3)_n$ cluster is defined as follows:

$$E_{\rm b} = -\frac{E_{\rm el}(({\rm Fe}_{2}{\rm O}_{3})_{n}) + E_{\rm ZPE}(({\rm Fe}_{2}{\rm O}_{3})_{n})) - [2nE({\rm Fe}) + 3nE({\rm O})]}{n},$$
(4)

where $E_{el}((Fe_2O_3)_n)$ and $E_{ZPE}((Fe_2O_3)_n)$ are the electronic and zero-point energies of a cluster $(Fe_2O_3)_n$ with a number of units *n*, while E(Fe) and E(O) are the energies of free Fe and O atoms, respectively.

The standard free energy of adsorption, ΔG_{ads} , is given as

$$\Delta G_{ads} = G(\mathrm{NH}_3@(\mathrm{Fe}_2\mathrm{O}_3)_n) - (G((\mathrm{Fe}_2\mathrm{O}_3)_n) + G(\mathrm{NH}_3)), \quad (5)$$

where $G(NH_3@(Fe_2O_3)_n)$ is the free energy of the most stable structure of the (Fe₂O₃)n cluster with the adsorbed ammonia molecule, $G(Fe_2O_3)_n$ is the free energy of the bare $(Fe_2O_3)n$ cluster, and $G(NH_3)$ is the free energy of a single ammonia molecule. The values of free energy G in (5) can be calculated as follows:

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$$G = E_{\rm el} + E_{\rm ZPE} - TS, \tag{6}$$

where $E_{\rm el}$ and $E_{\rm ZPE}$ are the electronic and zero-point energies of the 214 system, S is the entropy of the system, and T is the temperature. The 215 reported energies have been corrected for the basis set superposition 216 error (BSSE). 217

III. RESULTS AND DISCUSSION

In the present work, we systematically investigated the ammonia decomposition reaction mechanisms on (Fe₂O₃)_n clusters of various sizes *n*, where n = 1-4. First, we identified approximate reaction pathways for the interactions between NH3 molecules and the most stable isomers of $(Fe_2O_3)_n$ clusters using the AFIR technique. The obtained AFIR pathways were subsequently re-optimized along the minimum energy path using the Locally Updated Plane (LUP) method, without applying artificial forces. We calculated various reaction mechanisms and the stepwise dissociation⁵¹ of hydrogen atoms from nitrogen-containing compounds on Fe(III) oxide clusters, following the elementary steps,

$$\mathrm{NH}_3 +^* \to \mathrm{NH}_3^*, \qquad (7) \qquad 230$$

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$$NH_3^* \to NH_2^* + H^*$$
, (8) ²³¹

$$NH_2^* + H^* \to NH^* + 2H^*,$$
 (9) ²³²

$$NH^* + 2H^* \to N^* + 3H^*.$$
 (10) ²³³

Here, * denotes a free cluster, while the adsorbed intermediates on the surface of the $(Fe_2O_3)_n$ cluster are represented by * in the superscript.

Finally, the adsorbed hydrogen atoms on the $(Fe_2O_3)_n$ clusters can combine to produce molecular hydrogen (H₂),

$$NH^* + 2H^* \to NH^* + H_2,$$
 (11) ²³⁹

$$N^* + 3H^* \rightarrow N^* + H^* + H_2.$$
 (12) ²⁴⁰

This paper is organized as follows. We first discuss the structures of free clusters, followed by the adsorption of NH₃ on the most stable isomers of $(Fe_2O_3)_n$, n = 1-4, clusters. We then examine the complete dehydrogenation and H₂ formation processes for each cluster size.

A. Structure of $(Fe_2O_3)_n$ clusters with n = 1-4

Figure 1 demonstrates the most stable structures of small 247 $(Fe_2O_3)_n$ clusters with n = 1-4, as obtained in the present work using 248 249 the automated GRRM approach. A total of up to 60 isomer structures have been obtained for each cluster size n. The low-energy 250 isomers for each cluster size, along with their relative binding ener-251 gies, are presented in Figs. S2-S5. We found that the most stable 252 structure of the smallest Fe₂O₃ cluster is a nonet kite-like type with a 253 binding energy $E_{\rm b}$ = 362.7 kcal/mol. The kite-like structure is a com-254 monly studied configuration^{52,53} and was previously investigated by 255 Sierka *et al.*,⁵⁴ who observed the most stable spin configuration for 256 this structure to be S = 0. In contrast, we found that the lowest energy 257 structure corresponds to a nonet state with S = 4, while the singlet 258 259 kite-like structure is 0.62 kcal/mol less stable at the B3LYP/6-31+G* level of theory as shown in Table S1. This finding is also compared 260 with another hybrid functional, M06,55 and a range-separated func-261

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FIG. 1. Most stable structures of $(Fe_2O_3)_n$ clusters with n = 1-4. The values of the total spin S and the binding energy E_b of the clusters are mentioned in the legends.

tional with additional dispersion correction, wB97XD,⁵⁶ in Table S1. The results of our calculations show that the absolute binding energy of (Fe₂O₃)_{*n*} rapidly increases with the increasing cluster size *n* from 1 to 2 by 60.4 kcal/mol. However, further growth in the binding energy with the cluster size slows down, demonstrating a tendency for saturation as *n* increases.

²⁷⁰ B. Ammonia adsorption on (Fe₂O₃)_n clusters

The adsorption of ammonia on (Fe₂O₃)_n clusters is a crucial initial step in the whole dehydrogenation process. Figure 2 demonstrates the most stable adsorption configurations of the NH₃

molecule on $(Fe_2O_3)_n$ clusters with n = 1-4. The corresponding 274 basis set superposition error corrected free energies of adsorption 275 and Fe-N bond distances are shown in Table I at 0 K. Our cal-276 culations show that the adsorption of NH₃ on the smallest Fe₂O₃ 277 cluster is the most stable among all cluster sizes considered in this 278 study, with an adsorption free energy of -28.55 kcal/mol. This find-279 ing is corroborated by Mulliken charge analysis, which shows that 280 more electrons are shared between the lone pair of the N atom 281 and the 3d orbitals of Fe^{2+} for n = 1. Meanwhile, for larger clus-282 ter sizes with n = 2-4, which primarily contain Fe³⁺, the electron 283 density is more localized over the bonding region, as also reported 284 by Sierka et al.54 Therefore, bonding occurs with the nitrogen 285 lone pair. 286

Our theoretical analysis indicates that the adsorption energy ΔG_{ads} of ammonia on $(Fe_2O_3)_n$ clusters decreases from n = 1 to n = 3, followed by a slight increase for n = 4. A similar trend in the change of adsorption energy with the cluster size was reported by Zhou et al.⁵⁷ for Ru_n@CNT systems. We also compared the adsorption energy of NH₃ on different metal and metal oxides in Table I. The obtained NH₃ adsorption energies on $(Fe_2O_3)_n$ clusters are about 8 kcal/mol higher than the data reported by Zhang et al. for the Ru(0001) surface.⁵⁸ Moreover, the adsorption of NH₃ and NO_x on the γ -Fe₂O₃(111) surface was studied by Huang et al.⁵⁹ using periodic density functional calculations. They calculated adsorption energies on the octahedral and tetrahedral sites of y-Fe₂O₃(111) to be -2.13 and -21.68 kcal/mol, respectively. Similarly, our calculated NH₃ adsorption energies on (Fe₂O₃)_n clusters for n = 3 and n = 4 are close to the data reported by Huang et al.,⁵⁹ as the adsorption of NH₃ on the three-coordinated Fe³⁺ site resembles the tetrahedral site of y-Fe₂O₃(111), while the adsorption on the four-coordinated Fe³⁺ site resembles the octahedral site of γ -Fe₂O₃.

As mentioned above, the calculated adsorption energies indicate that the adsorption of an NH_3 molecule on $(Fe_2O_3)_n$ clusters



FIG. 2. Optimized geometries of NH₃ adsorbed on $(Fe_2O_3)_n$ clusters for n = 1-4. N–Fe distances (Å) are shown in parentheses, along with the partial atomic charges on neighboring atoms. The values of the total spin *S* of the clusters are mentioned in the legends.

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313 TABLE I. NH₃ adsorption free energy ΔG_{ads} and d(Fe–N) bond length in various 314 sizes of $(Fe_2O_3)_n$, where n = 1-4.

(= =)			
	ΔG_{ads} (kcal/mol)	Fe–N (Å)	Reference
NH ₃ /Fe ₂ O ₃	-28.55	2.11	
$NH_3/(Fe_2O_3)_2$	-28.36	2.14	This work
$NH_3/(Fe_2O_3)_3$	-27.65	2.15	
$NH_3/(Fe_2O_3)_4$	-27.85	2.14	
NH ₃ /ZnFe ₂ O ₄ (110)	-48.54	Zn-N (2.03)	a
	-41.52	Fe-N (1.99)	
NH ₃ /Ru(0001)	-20.52	Ru–N (2.17)	b
NH ₃ /Fe ₂ O ₃ /AC	-49.12, -37.35		с
	-26.29, -31.13		
NH3/y-Fe2O3 nano	-37.52		d
$\frac{1}{NH_2/\nu - Fe_2O_2(111)}$	-21.68	Fe _{tet} -N (2.13)	e
	-2.13	$Fe_{oct} - N(2.101)$	

Reference 60.

^bReference 58. 334 335 ^cReference 61.

^dReference 62. 336

337 ^eReference 59.

> (n = 1-4) weakens as the cluster size increases from n = 1 to n = 3. In industrial processes, the dehydrogenation of ammonia typically occurs at high temperatures, often in the range of 400-700 °C, depending on the specific catalysts and conditions used. Therefore, it is important to determine the range of temperatures at which ammonia adsorption on $(Fe_2O_3)_n$ remains stable. Figure 3 demonstrates the temperature dependence of ΔG_{ads} in the range from 0 to 1200 K for the most stable adsorption configurations of NH_3 on $(Fe_2O_3)n$ clusters (n = 1-4). The negative values of ΔG_{ads} correspond to stable adsorption. As shown in Fig. 3, NH₃ adsorbed on the smallest Fe₂O₃ cluster is stable across the whole range of the considered



FIG. 3. Temperature dependence of the adsorption free energy for NH₃ adsorption on $(Fe_2O_3)_n$ clusters with n = 1-4 at 1 atm.

temperatures. However, for larger cluster sizes, ammonia adsorption 351 becomes energetically unfavorable at temperatures of 1140 (K), 940 352 (K), and 989 (K) for *n* = 2, 3, and 4, respectively. 353

C. NH₃ decomposition on Fe₂O₃

Here, we discuss the complete NH3 decomposition and H2 formation reactions (7)–(12) on the smallest considered cluster, Fe₂O₃, at room temperature, T = 298.15 K, explored by the AFIR method. This method allows for the automatic exploration of the full reaction path network, systematically accounting for the variety of possible isomer structures and adsorption sites. This is an important approach in nanocatalysis because it has been demonstrated that the most stable structures are not always the most reactive. Therefore, a systematic search for reaction pathways that accounts for the contributions of low-energy isomers is required to accurately describe the catalytic properties of clusters at finite temperatures.⁴

To illustrate the isomer and reaction-site effects, we explicitly consider two different isomers of the Fe₂O₃ cluster: the most stable kite-like structure with one terminal oxygen atom and the linear structure isomer with two terminal oxygen atoms, which is 6.24 kcal/mol less stable (see Fig. S2). The kite-like structure possesses two types of catalytically active metal centers-two-coordinated and three-coordinated Fe sites. Therefore, we consider the adsorption and decomposition of an NH3 molecule on both of them.

Figure 4(a) demonstrates that the adsorption of NH₃ on the kite-like Fe₂O₃ cluster is an exothermic reaction, occurring at both the two-coordinated and three-coordinated Fe sites. The adsorption free energies are -21.85 kcal/mol for the two-coordinated Fe site (intermediate I'_{11}) and -8.75 kcal/mol for the three-coordinated Fe site (intermediate I_1'' 1). The optimized structures of all intermediates (I) and transition states (T) along the reaction pathways are shown in Figs. 4(b) and 5(b), for the kite-like and linear clusters, respectively. Here, the lower index corresponds to the cluster size *n*, while the numbering corresponds to the order of intermediates(transition states) along the reaction path. As discussed in Sec. III B, the most stable adsorption site for NH3 is the two-coordinated Fe site, with an Fe-N bond length of 2.11 Å. In contrast, the Fe-N bond length at the three-coordinated Fe site is 2.16 Å. These findings are supported by the fact that NH₃ adsorption highly depends on the local geometry and electronic structure of the catalyst.

In the case of the Fe₂O₃ kite-like structure, the first dehydrogenation reaction is the second step in the reaction mechanism, occurring after adsorption with the activation barriers of 21.85 kcal/mol and 19.58 kcal/mol through the reaction paths $I'_1 I - T'_1 I - I'_1 2$ and $I''_1 I - T''_1 I - I''_1 2$, respectively. The reactions on these two-coordinated and three-coordinated active sites are exothermic by 21.44 and 10.07 kcal/mol, respectively. However, the first dehydrogenation of NH₃ on the linear-type structure [Fig. 5(a)] occurs with a smaller activation barrier of 13.96 kcal/mol via the reaction path $I_1^L 1 - T_1^L 1 - I_1^L 2$, demonstrating that the less stable linear isomer is more reactive.

The role of the Fe₂O₃ isomer structure on NH₃ adsorption and the first hydrogen atom transfer was previously studied by Xie et al.⁶¹ They performed DFT-D3 calculations on the adsorption mechanisms of different molecules (NH₃, NO, and O₂) on activated carbon (AC) supported iron-based catalysts Fe_xO_v/AC . The calculated adsorption electronic energies of NH3 were -37.4 and -53.7

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FIG. 4. (a) Energy profile for the $NH_2^* \rightarrow NH_2^* + H^*$ \rightarrow NH* + 2H* \rightarrow N* + 3H* reaction path on the kite-like isomer of Fe_2O_3 at T = 298.15 K. (b) Geometries of the optimized equilibrium and transition states along the reaction path

FIG. 5. (a) Energy profile for the $NH_3^* \rightarrow NH_2^* + H^*$ 428 \rightarrow NH* + 2H* \rightarrow N* + 3H* reaction path on the lineartype isomer of Fe_2O_3 at T = 298.15 K. (b) Geometries of the optimized equilibrium and transition states along the reaction path. 432

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kcal/mol on different isomers of Fe₂O₃/AC, and the first hydrogen atom transfer had an activation barrier of 15.5 kcal/mol. Similarly, the adsorption and dehydrogenation of ammonia on different metal oxides were investigated by Erdtman and co-workers⁶³ for the application of gas sensors. They reported that the adsorption energy of NH3 on the RuO2(110) surface is -38.24 kcal/mol, and the first N-H bond cleavage had an activation energy barrier of 17.45 kcal/mol.

 $(T_{1}^{L}3)$

 $(T^{L}_{1}4)$

 $(T_{1}^{L}5)$

(T^L₁2)

The third step of the NH₃ dehydrogenation reaction (9) involves the dissociation of the adsorbed NH₂^{*} intermediate into NH^{*} and H^{*} species. In this step, the abstracted hydrogen atom transfers to one of the oxygen atoms in the cluster. Figure 4(a)demonstrates that in the case of the kite-like structure, the energy barriers for this step are 43.91 and 34.51 kcal/mol, corresponding to the reaction paths $I'_{1}2-T'_{1}2-I'_{1}3$ and $I''_{1}2-T''_{1}2-I''_{1}3$.

In the fourth step (10), the adsorbed NH^{*} intermediate further dissociates into N^* and H^* species as shown in Fig. 4(a). The reaction barriers associated with this step are 46.98 and 8.95 kcal/mol for the two-coordinated and three-coordinated reaction paths, respectively. The decomposition of NH3 on kite-like structures becomes endothermic starting from the third step (9). Our calculations reveal that NH₃ dehydrogenation has a high energy barrier when the NH₃ molecule is adsorbed at a two-coordinated Fe site, which is the most stable adsorption site. Meanwhile, the dehydrogenation of the adsorbed NH3 at a three-coordinated Fe site has a considerably lower activation barrier of 8.95 kcal/mol for the reaction step (10).

Overall, for the NH₃ decomposition reaction on the kite-like Fe₂O₃ structure, with initial NH₃ adsorption on the two-coordinated Fe atom, the rate-limiting step is the fourth reaction (10), with a barrier of 46.98 kcal/mol. Alternatively, for the less favorable NH₃ adsorption on the three-coordinated Fe atom, the rate-limiting step is the third reaction step (9), with a barrier of 34.51 kcal/mol.

The reaction pathway calculated for NH₃ decomposition on the linear-type Fe_2O_3 isomer is shown in Fig. 5(a), and respective

 $(T_{1}^{L}1)$



intermediate and transition state structures are shown in Fig. 5(b). Since this structure consists of two iron atoms connected through a central oxygen, each containing a terminal oxygen, the reaction mechanism differs slightly from that of the kite-like isomer. For instance, in the third step of the reaction, the second hydrogen from the adsorbed $\rm NH_2^*$ intermediate is transferred to the second terminal oxygen. The energy barrier for this step on the linear-type

structure is 23.8 kcal/mol, as shown in the reaction path $(I_1^L 2 - T_1^L 2 - I_1^L 3)$ in Fig. 5(a).

The fourth step on this isomer is not straightforward, involving the central oxygen atom breaking its bond with one of the neighboring iron atoms while forming an Fe–N–Fe bridge. This process leads to two different intermediates: the formation of the adsorbed H_2O^* and the transfer of a hydrogen atom from one side of the Fe–N–Fe 470

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bridge to the other. Subsequently, the final dehydrogenation step
from the NH* intermediate occurs, with an activation energy barrier
of 34.76 kcal/mol.

474 As a next step, we consider possible H_2 formation via reac-475 tions (11) and (12) on the kite-like and linear isomers of the 476 Fe₂O₃ cluster. The possible pathways for H_2 formation in the case 477 of the most stable ammonia adsorption on the two-coordinated 478 site (I' intermediates) of the kite-like Fe₂O₃ isomer are shown in 479 Fig. 6(a), while the corresponding structures of the optimized equi-480 librium and transition states along the reaction path are illustrated in 479 Fig. 6(b).

481 Note that H₂ formation can occur after the partial decompo-482 sition of ammonia in reaction (11), starting from the intermediate $(I_1^I 3)$ via the path $I_1^\prime 3 - T_1^\prime 6 - I_1^\prime 7 - T_1^\prime 7 - I_1^\prime 8$. Meanwhile, H_2 formation 483 can occur via the full decomposition of ammonia in reaction (12), 484 485 through the intermediate $(I_1^I 4)$ via the path $I_1' 4 - T_1' 4 - I_1' 5 - T_1' 5 - I_1' 6$. In 486 both cases, the reaction pathways include breaking one O-H bond 487 and forming an Fe-H bond. The H₂ formation barriers through these intermediates are 89.74 and 92.49 kcal/mol, respectively. From 488 489 these results, we conclude that H₂ formation on the kite-like Fe₂O₃ structure is more favorable via reaction (11), with the NH^{*} interme-490 491 diate remaining adsorbed on the cluster. The H₂ formation reaction, starting from $(I_1^I 4)$, is the rate-limiting step in molecular hydrogen 492 493 formation on the kite Fe₂O₃ cluster.

494 Similarly, the H_2 formation reaction pathways on the linear-495 type structure of Fe_2O_3 are shown in Fig. 7(a), while the optimized equilibrium and transition states along the reaction path 498 are illustrated in Fig. 7(b). The H₂ formation through the NH* inter-499 mediate $(I_1^L 4)$ via the reaction path $I_1^L 4 - T_1^L 8 - I_1^L 9 - T_1^L 9 - I_1^L 10$ has an 500 energy barrier of 79.99 kcal/mol. Meanwhile, H₂ formation through 501 the intermediate $(I_1^L 6)$ via the reaction path $I_1^L 6 - T_1^L 6 - I_1^L 7 - T_1^L 7 - I_1^L 8$ 502 has an activation energy of 70.84 kcal/mol, which is about 503 10 kcal/mol lower energy than the reaction path through the 504 intermediate $(I_1^L 4)$. 505

Overall, our calculated reaction pathways for H_2 formation show a similar pattern for both kite-type and linear-type Fe₂O₃, where H_2 formation in reactions (11) and (12) take place via breaking one O–H bond and forming an intermediate Fe–H bond. However, from both thermodynamic and kinetic perspectives, H_2 formation on the two types of Fe₂O₃ structures varies. Reaction (11) is more favorable on the kite-like structure, while reaction (12) is more favorable on the linear structure. This highlights that the ratelimiting step for H_2 formation is highly dependent on the catalyst's structure.

D. NH₃ decomposition on Fe₄O₆

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In Subsection III E, we discuss the catalytic activity of $(Fe_2O_3)_2$ • \mathfrak{GP} toward NH₃ dehydrogenation and H₂ formation reactions. On the basis of adsorption characteristics discussed in Sec. III B, the threefold coordinate Fe³⁺ site of the Fe₄O₆ cluster is the most stable site for NH₃ adsorption. A complete reaction pathway for the stepwise 521



FIG. 8. (a) Energy profile for the $NH_3^* \rightarrow NH_2^* + H^* \rightarrow NH^* + 2H^* \rightarrow N^* + 3H^*$ and H_2 formation reaction paths on the (Fe₂O₃)₂ cluster at T = 298.15 K. (b) Geometries of the optimized equilibrium and transition states along the reaction path.

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FIG. 9. (a) Energy profile for the NH₃^{*} \rightarrow NH₂^{*} + H^{*} \rightarrow NH^{*} + 2H^{*} \rightarrow N^{*} + 3H^{*} and H₂ formation reaction paths on the (Fe₂O₃)₃ cluster at T = 298.15 K. (b) Geometries of the optimized equilibrium and transition states along the reaction path.

524 decomposition of NH₃ and the formation of H₂ reactions on the 525 $(Fe_2O_3)_2$ cluster is depicted in Fig. 8(a), and the corresponding 526 intermediate and transition state structures are shown in Fig. 8(b). 527 From this point forward, the first dehydrogenation step follows 528 starting from the intermediate (I21), where the NH3 molecule inter-529 acts with the three-coordinated Fe site of the (Fe₂O₃)₂ cluster by 530 transferring a hydrogen to its one of neighboring oxygens via the 531 reaction pathway (I₂1-T₁1-I₂2) and the reaction barrier of this 532 step is 23.35 kcal/mol, which is 1.5 kcal/mol higher energy bar-533 rier than the first hydrogen transfer on the kite-like Fe₂O₃ cluster. 534 This reaction also involves different isomers of (Fe₂O₃)₂, where 535 decomposition takes place on the second minima isomer of (Fe₂O₃)₂ 536 shown in Fig. S3. The relative binding energy of the second minima 537 isomer is 2.35 kcal/mol. The second dehydrogenation step that fol-538 lows from the adsorbate NH^{*}₂ intermediate (I₂2) further dissociates 539 to NH^{*} + 2H^{*}, in which the dissociated hydrogen atom is subse-540quently transferred to another neighboring oxygen as shown in the 541 reaction path $(I_22-T_22-I_23)$. This reaction occurs with an energy 542 barrier of 38.57 kcal/mol. The ultimate dehydrogenation step is the 543 formation of $N^* + 3H^*$, where N is bound to the central top Fe³⁺ 544 and all the hydrogen atoms interact with three neighboring oxygens. 545 The last dehydrogenation step occurs with an energy barrier of 3.86 546 kcal/mol higher than the energy barrier of the second dehydrogena-547 tion step, and it is shown in the reaction pathway $(I_23-T_23-I_24)$. 548 It suggests that the dehydrogenation of adsorbate NH* is a rate-549 determining step on the (Fe₂O₃)₂ cluster. Moreover, from a ther-550 modynamic viewpoint, the calculated dehydrogenation steps of

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 NH_3 on the (Fe₂O₃)₂ cluster are endothermic by 8.12, 18.6, and 23.78 kcal/mol.

We consider the H_2 formation reactions via two reaction pathways. The first H_2 formation reaction (11) occurs with the partial decomposition of NH_3 starting from intermediates (I₂3) through (I₂9). In the first stage through this reaction path starting from (I₂3), the transition state (T₂6) was found, where the H atom adsorbed onto the Fe atom, forming an Fe–H bond. In the second stage of the reaction, the transition state (T₂7) was the one that splits the adsorbed H atom from the adjacent O atom to form adsorbed NH^{*}. Then, the dissociated H atom was adsorbed onto the O atom, which is an adjacent atom to the Fe–H bond, and at the final stage, the dissociative molecular H₂ formed via (T₂8), and the barrier of this reaction is 91.1 kcal/mol.

The complete reaction pathway for reaction (11) is $(I_23-T_26-I_27-T_27-I_28-T_28-I_29)$. The second H₂ formation reaction (12) occurs with the fully decomposed NH₃ molecule starting from the intermediate (I₂4) through the intermediate (I₂6). It is important to note that the last dehydrogenation reaction (10) is the one that has the highest barrier on the (Fe₂O₃)₂ cluster. So, the dissociative molecular hydrogen formation through this reaction path costs an energy as shown in the reaction path (I₂4-T₂4-I₂5-T₂5-I₂6). Overall, as it seen from the depicted reaction pathways in Fig. 8, the H₂ formation reaction is kinetically and energetically costly in the reaction N^{*} + 3H^{*} \rightarrow N^{*} + H^{*} + H₂, which is the partial decomposition of NH₃ on the (Fe₂O₃)₂ cluster.

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578 E. NH₃ decomposition on Fe₆O₉

The energy profile for the stepwise dehydrogenation of NH₃ on 579 580 the $(Fe_2O_3)_3$ cluster is presented in Fig. 9(a), while the intermediate 581 and transition state structures along this reaction pathway are shown 582 in Fig. 9(b). The dissociation of NH_3 on the $(Fe_2O_3)_3$ cluster is more 583 complex compared to smaller Fe(III) oxide structures, as NH₃ can 584 adsorb at various sites on the $(Fe_2O_3)_3$ surface.

585 We identified the most favorable adsorption configuration, I₃1, 586 with an adsorption energy of $\Delta G = -18.8$ kcal/mol, from which 587 the stepwise decomposition reaction proceeds. The first dehydro-588 genation reaction, as described in (8), begins with NH₃^{*} adsorbed 589 on the $(Fe_2O_3)_3$ cluster as I_31 and proceeds through the transition 590 state T₃1. The energy barrier along this pathway is 20.04 kcal/mol, which is lower than the barrier for the first H abstraction from 591 592 NH_3 on the $(Fe_2O_3)_2$ cluster. Although the first dehydrogenation reaction on the $(Fe_2O_3)_3$ cluster is endothermic, we observed that 593 594 when the NH^{*}₂ species migrates to a bridging position between two Fe atoms (Fe-N-Fe), the reaction becomes exothermic by 595 596 14.15 kcal/mol, as shown in the reaction pathways I₃2-T₃2-I₃3 and I33-T33-I34. 597

598 The second H abstraction involves a further dehydrogenation 599 of NH₂^{*} into NH^{*} and H^{*}, with an energy barrier of 35.97 kcal/mol 600 along the pathway I₃4-T₃4-I₃5. This barrier is 15.96 kcal/mol higher 601 than that of the first dehydrogenation step. In addition, this reaction 602 is endothermic, with a reaction energy of 15.74 kcal/mol.

603 Similarly, in the third step (10), the remaining NH^{*} dissociates 604 into N* and H*, with an energy barrier of 17.94 kcal/mol higher 605 than that of the second dissociation step. This is the largest barrier 606 encountered in the decomposition of NH₃. The calculated reaction

pathway indicates that this process is endothermic, with a reaction energy of 25.76 kcal/mol.

Finally, the possible H_2 formation reactions [(11) and (12)] on the (Fe₂O₃)₃ cluster were calculated, as shown in Fig. 9. The first H₂ formation reaction (11) begins with one adsorbed NH* and two H^* species on the (Fe₂O₃)₃ cluster. The reaction proceeds in a manner similar to that discussed in Subsection III D: the adsorbed Q73 H* on oxygen, adjacent to NH* adsorbed on Fe, migrates away by forming Fe–H bonds through the transition states T_37 and T_38 . The overall energy barrier for H_2 formation via reaction (11) is 100.74 kcal/mol.

The second possible H₂ formation pathway starts from fully decomposed NH₃ (I₃6) and proceeds through the transition state T₃6. This pathway has a significantly high energy barrier, calculated to be 116.89 kcal/mol, as shown in the reaction path I₃6-T₃6-I₃7. These results suggest that, from both a thermodynamic and a kinetic perspective, H₂ formation after full dehydrogenation of NH₃ is less favorable.

F. NH₃ decomposition on Fe₈O₁₂

Finally, the decomposition of NH3 and the H2 formation path-626 ways on the $(Fe_2O_3)_4$ cluster is illustrated in Fig. 10(a), with the 627 intermediate and transition state structures shown in Fig. 10(b). 628 As discussed in Secs. III A-III E, increasing the number of units 629 *n* in $(Fe_2O_3)_n$ increases the number of active sites that interact 630 with NH₃. However, similar to the reactions on $(Fe_2O_3)_n$ (n = 2, 3), 631 the most stable adsorption site for NH₃ on (Fe₂O₃)₄ is a three-632 coordinated Fe site, with an adsorption energy of -19.2 kcal/mol 633



FIG. 10. (a) Energy profile for the $NH_3^* \rightarrow NH_2^* + H^*$ \rightarrow NH* + 2H* \rightarrow N* + 3H* and H₂ formation reaction paths on the $(Fe_2O_3)_4$ cluster at T = 298.15 K. (b) Geometries of the optimized equilibrium and transition states along the reaction path

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at room temperature, slightly higher than that on $(Fe_2O_3)_3$. The 639 640 dehydrogenation of NH₃ begins with the adsorption of NH₃^{*}, as 641 shown in the intermediate state I₄1. The first dehydrogenation step 642 involves breaking one N-H bond and forming an O-H bond, with an energy barrier of 19.74 kcal/mol, as shown in the reaction path-643 644 way $I_41-T_41-I_42$. The second dehydrogenation step (9) involves the 645 dissociation of $NH_2^* + H^*$ to form $NH^* + 2H^*$, proceeding through 646 the transition state T₄2. The energy barrier for this step is 43.96 647 kcal/mol, which is higher than the corresponding second dehydro-648 genation steps on $(Fe_2O_3)_n$ (n = 1-3). The final dehydrogenation 649 step occurs along the pathway $I_43-T_43-I_44$, with a barrier of 42.24 650 kcal/mol. All NH₃ dehydrogenation steps on (Fe₂O₃)₄ are endother-651 mic, with reaction energies of 1.11, 15.39, and 41.47 kcal/mol, 652 respectively.

The final reaction pathway on the $(Fe_2O_3)_4$ cluster involves H₂ formation from both partially and fully decomposed NH₃, as described in (11) and (12). As observed for all sizes of $(Fe_2O_3)_n$ clusters, H₂ formation is energetically more favorable after the partial decomposition of NH₃ in reaction (11) compared to the fully decomposed pathway (12). However, this pathway also presents the highest energy barrier on this cluster.

660 IV. COMPARISON AND CONCLUSION

Our results, illustrated in Figs. 4, 5, and 8–10, indicate that NH₃ dehydrogenation can be a thermodynamically favorable reaction on (Fe₂O₃)_n (n = 1-4) clusters. However, the favorability depends on the size and geometry of the cluster, as well as the specific reaction steps described in (8)–(12).

To compare the activity of various sizes and structures of $(Fe_2O_3)_n$ (n = 1-4), we have calculated the change in Gibbs free energy (ΔG) as a function of temperature at 1 bar pressure, as shown in Fig. S6. Across all reactions studied, we observed that ΔG increases with temperature. This suggests that NH₃ dehydrogenation on $(Fe_2O_3)_n$ (n = 2, 4) can be energetically favorable at moderate temperatures, depending on the specific reaction step. However, as the temperature rises beyond a certain threshold, the reaction becomes unfavorable.

For example, as shown in Figs. S6(a)-S6(c), all dehydrogenation reactions on $(Fe_2O_3)_n$ (n = 1) are energetically favorable within the temperature range of 0-1000 K. In contrast, on $(Fe_2O_3)_n$ (n = 2, 4), only the last dehydrogenation step is limiting. Since ΔG of the third dehydrogenation reaction is already greater than zero at 0 K, this step is not favorable at any temperature. Another larger cluster considered in this study, $(Fe_2O_3)_n$ (*n* = 3), exhibits better stability of the reaction intermediates during the second dehydrogenation step, remaining favorable up to 800 K. Meanwhile, the second dehydrogenation reaction on $(Fe_2O_3)_n$ (n = 4) is favorable only up to 400 K. The most endothermic dehydrogenation reaction on this cluster is the step $NH^* + 2H^* \rightarrow N^* + 3H^*$. The first and second dehydrogenation steps are favorable up to 1100 and 700 K, respectively. Moreover, we observed the variation in ΔG with temperature for the H₂ formation reaction on $(Fe_2O_3)_n$ (n = 1-4). Our results indicate that the formation of molecular hydrogen is not thermodynamically favorable at any temperature. However, temperature is not the only factor determining whether the reaction occurs. If sufficient energy is available to overcome the activation barrier, the reaction can still proceed.

The effective production of molecular hydrogen from ammonia is determined by the stepwise dehydrogenation of adsorbed ammonia on the catalyst. Catalytic reaction mechanisms are analyzed by identifying the rate-determining step in the dehydrogenation of NH₃, which corresponds to the step requiring the highest energy to activate the N–H bond. However, it is important to note that in catalysis, the overall energy barrier is more significant than the barrier for any single intermediate reaction step.

Several studies have reported different rate-determining steps 703 depending on the type of catalyst used.⁶⁴ Lu et al. found that the 704 rate-determining step in NH3 decomposition on different phases of 705 Ru surface catalysts is the formation of molecular nitrogen.⁶⁵ In con-706 trast, studies by Zhang et al.¹⁹ on ammonia decomposition on small 707 iron clusters showed that the rate-determining step on single Fe and 708 Fe₃ is the NH^{*} \rightarrow N^{*} + H^{*} step, whereas for Fe₂ and Fe₄, the rate-709 determining step is the $NH_2^* \rightarrow NH^* + H^*$ step. Similarly, a detailed 710 comparison of the energy barriers for each elementary step in NH₃ 711 decomposition and H₂ formation on different sizes and shapes of 712 $(Fe_2O_3)_n$ (n = 1-4) is shown in Fig. 11. Based on the results from 713 our calculations, the rate-determining step in ammonia decomposi-714 tion and H₂ formation varies with the size of the $(Fe_2O_3)_n$ (n = 1-4)715 oxide clusters. In general, the final step of H₂ formation represents 716 the highest energy barrier on all $(Fe_2O_3)_n$ (n = 1-4) clusters. How-717 ever, the analysis of NH₃ decomposition shows that the NH^{*} \rightarrow N^{*} 718 + H* step is typically the rate-determining step, except in the case 719 of (Fe₂O₃)₄, where the rate-determining step is the second H disso-720 ciation step. Furthermore, the first dehydrogenation step exhibits an 721 energy barrier that is nearly identical across all clusters, with the pro-722 cess being exothermic for clusters n = 1 and n = 3 and endothermic 723 for clusters n = 2 and n = 4. For the second dehydrogenation step, 724 (Fe₂O₃)₃ demonstrates a significantly higher activity compared to 725 the other cluster sizes. It is also important to note that n = 1 (linear) 726 is the only special configuration of Fe₂O₃ containing two terminal 727 O^{-2} ions, unlike the other types of Fe₂O₃, which may promote a 728 potentially high activity for NH3 dehydrogenation and molecular 729 hydrogen formation. Overall, the lowest energy barrier observed for 730 H₂ formation is associated with the largest cluster considered in this 731 study. 732 733

In this research, various structures of $(Fe_2O_3)_n$ (n = 1-4) were obtained using the SC-AFIR method, and we investigated the ammonia decomposition and molecular hydrogen formation reaction pathways on the most stable isomers of $(Fe_2O_3)_n$ (n = 1-4)clusters. This analysis employed the SC-AFIR and DS-AFIR methods within the Global Reaction Route Mapping (GRRM) strategy, utilizing the B3LYP exchange–correlation functional in Kohn–Sham DFT.

The results indicate that the catalytic activity in ammonia 740 decomposition varies depending on the size and shape of the high-741 spin iron trioxides. The adsorption analysis reveals that the NH₃ 742 molecule preferentially adsorbs at two-coordinated Fe sites in n = 1743 and at three-coordinated Fe sites in n = 2-4 clusters. Furthermore, 744 the adsorption energy tends to decrease from n = 1 to n = 3 of the 745 $(Fe_2O_3)_n$ clusters and then slightly increases for the $(Fe_2O_3)_4$ clus-746 ter. From a thermodynamic perspective, the adsorption of the NH₃ 747 molecule on Fe₂O₃ is favorable across the whole range of the con-748 749 sidered temperatures from 0 to 1200 K. In contrast, for the larger clusters $(Fe_2O_3)_n$ (n = 2, 4), ammonia adsorption becomes energeti-750 751 cally unfavorable at temperatures of 1140, 940, and 989 K for n = 2, 3,

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FIG. 11. Reaction barrier (ΔG^{\ddagger}) for NH₃ dehydrogenation and H₂ formation reactions on (Fe₂O₃)_n (n = 1–4) clusters.

and 4, respectively. A comparison of the rate-determining steps in the ammonia dehydrogenation reaction reveals a dependency on the size of the iron trioxide clusters. Thus, the reaction step NH^{*} \rightarrow N^{*} + H^{*} is the rate-determining step for the smaller iron trioxide clusters (Fe₂O₃)_n (*n* = 1–3). In contrast, the reaction step NH^{*}₂ \rightarrow NH^{*} + H^{*} is identified as the rate-determining step for the (Fe₂O₃)_n (*n* = 4) cluster. In addition, we observed that the energy barrier for molecular hydrogen formation increases with the size of the clusters (Fe₂O₃)_n (*n* = 1–3) but then experiences a drastic decrease for the (Fe₂O₃)₄ cluster.

We have investigated the catalytic activity of high-spin $(Fe_2O_3)_n$ (n = 1-4) clusters for the decomposition of NH₃. We believe that the results are valuable for designing iron trioxide-based nanosized catalysts by regulating the size of the $(Fe_2O_3)_n$ clusters to enhance H₂ production from the catalytic decomposition of ammonia.

SUPPLEMENTARY MATERIAL

The supplementary material provides the energies and structures of the lowest-energy isomers of $(Fe_2O_3)_n$ (n = 1-4) clusters and the change in Gibbs free energy with temperature for each dehydrogenation step.

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DFT calculations.	788

AUTHOR DECLARATIONS

Confli	ct of	Interest
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The authors have no conflicts to disclose.

Author Contributions

Sapajan Ibragimov: Data curation (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). Andrey Lyalin: Conceptualization (equal); Supervision (equal); Writing – review & editing (equal). Sonu Kumar: Investigation (equal); Writing – review & editing (equal). Yuriko Ono: Methodology (equal); Writing – review & editing (equal). Tetsuya Taketsugu: Supervision (equal); Writing – review & editing (equal). Maciej Bobrowski: Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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