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# Iron oxide cluster induced barrier-free conversion of nitric oxide to ammonia<sup>†</sup>

Keisuke Takahashi<sup>\*a</sup>

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**Nitrogen oxide (NO) conversion to ammonia (NH<sub>3</sub>) over iron oxide cluster is investigated within the density functional theory calculation. The introduction of NO and H<sub>2</sub> over gas-phase Fe<sub>4</sub>O<sub>2</sub> results in the formation of NH<sub>3</sub> and H<sub>2</sub>O without activation barriers. The key reaction is barrier free conversion of NO to N and H<sub>2</sub>O where the physical origin rests on negative-negative repulsion of NO over iron oxide clusters. The by-product H<sub>2</sub>O can be a hydrogen source by electrolysis or re-visiting Fe<sub>4</sub>O<sub>2</sub>, hence, the reaction is self-sustainable. Furthermore, the above reactions are performed depositing Fe<sub>4</sub>O<sub>2</sub> cluster on graphene/Cu(111) where the barrier free conversion of NO to NH<sub>3</sub> is also observed, predicting that such reaction can be applicable. Thus, low temperature conversion of NO to NH<sub>3</sub> over Fe<sub>4</sub>O<sub>2</sub> can be predicted. The detailed reaction path and mechanism are presented.**

Ammonia (NH<sub>3</sub>) is a key chemical compound used when addressing the growing human population and its demands for food as its primary use is towards the production of fertilizers<sup>1</sup>. Ammonia synthesis is a prototype reaction in heterogeneous catalysts and extensively investigated because of technological and social importances<sup>2-4</sup>. The Haber-Bosch process is a successful process used to synthesize ammonia from nitrogen and hydrogen gas. However, the reaction requires high pressure and high temperature in order to maintain the reaction and dissociate N<sub>2</sub> as N<sub>2</sub> has a strong triple bond. Tremendous amounts of catalysts were screened where Fe based catalysts were found to accelerate the reaction process; however, the reaction still takes place at high temperature<sup>5</sup>. Sustainable production of ammonia is a critical matter for efficient food production. Here, nitric oxide (NO) gas is proposed as a nitrogen source for ammonia production instead of N<sub>2</sub> gas in order to seek low temperature reactions.

NO is an undesirable chemical compound that is produced from automobile exhaust, fossil fuel plants, and industrial factories. NO is considered to be the origin of countless environmental issues including acid rain, ozone depletion, and photo-

chemical smog<sup>6</sup>. Thus, the reduction of NO has been extensively investigated including the selective catalytic reduction<sup>7</sup>. In general, NO reduction is performed with NH<sub>3</sub> and O<sub>2</sub> over catalysts where H<sub>2</sub>O and N<sub>2</sub> are produced at relatively high temperature<sup>8</sup>. Passive selective catalytic reaction is a newly introduced technology where NH<sub>3</sub> is generated from the reaction of NO and H<sub>2</sub> over catalysts within the selective catalytic reaction<sup>9</sup>. This suggests that NO can be a potential candidate as a nitrogen source for ammonia production if the dissociation of NO can occur and sufficient amount of ammonia can be produced.

Iron oxide clusters are proposed as a potential catalyst for converting NO to NH<sub>3</sub> as the catalytic effect of iron oxide clusters have found to be effective towards NO reduction and CO oxidation<sup>10,11</sup>. In particular, the Fe<sub>4</sub>O<sub>2</sub> cluster is investigated as such clusters are able to be synthesized within experiments where synthesis of Fe<sub>4</sub>O<sub>2</sub> clusters is experimentally generated by using a laser vaporization and analysis conducted by photoelectron spectroscopy<sup>12</sup>. Furthermore, for practical applications, the conversion of NO to NH<sub>3</sub> over supported Fe<sub>4</sub>O<sub>2</sub> clusters is studied. In particular, Fe<sub>4</sub>O<sub>2</sub> clusters are deposited on a single layer graphene/Cu(111) where graphene/Cu(111) is experimentally producible as graphene can preserve the properties and structures of Fe clusters<sup>13,14</sup>.

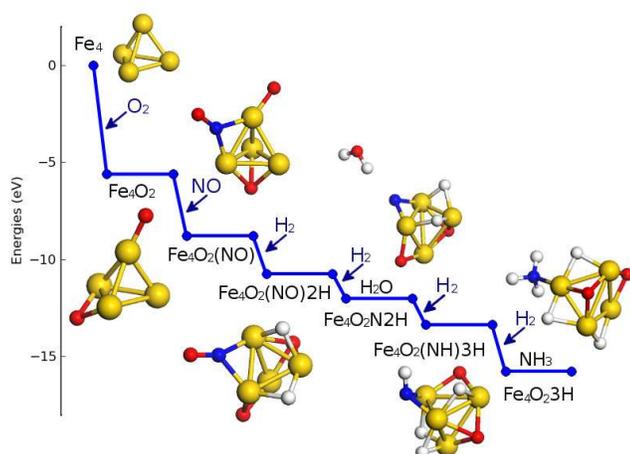
Here, a novel reaction path of the conversion of NO to NH<sub>3</sub> with Fe<sub>4</sub>O<sub>2</sub> clusters is proposed. The reaction step is screened and investigated by using the density functional theory calculation in order to reveal the precise reaction path.

The grid-based projector-augmented wave (GPAW) method is implemented within density functional theory<sup>15</sup>. The exchange correlation of PBE and vdW-DF are applied for gas-phase and supported cluster case, respectively<sup>16,17</sup>. The ground state structure of gas phase and supported Fe<sub>4</sub> clusters are searched by implementing the basin-hopping algorithm<sup>14,18</sup>. See Supporting Information for further details.

The conversion of NO to NH<sub>3</sub> over gas phase Fe<sub>4</sub> is investigated. The reaction path with corresponding atomic models and adsorption energies is shown in Figure 1. The ground state structure of gas phase Fe<sub>4</sub> is found to have a pyramidal structure. The structure and spin multiplicity of Fe<sub>4</sub> have

<sup>†</sup> Electronic Supplementary Information (ESI) available:

<sup>a</sup> Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo 060-8278, Japan. E-mail: keisuke.takahashi@eng.hokudai.ac.jp



**Fig. 1** The reaction path of the conversion of NO to NH<sub>3</sub> over the gas phase Fe<sub>4</sub> clusters with corresponding adsorption energies. Atomic color codes: Fe, yellow; O, red; N, blue; H, white.

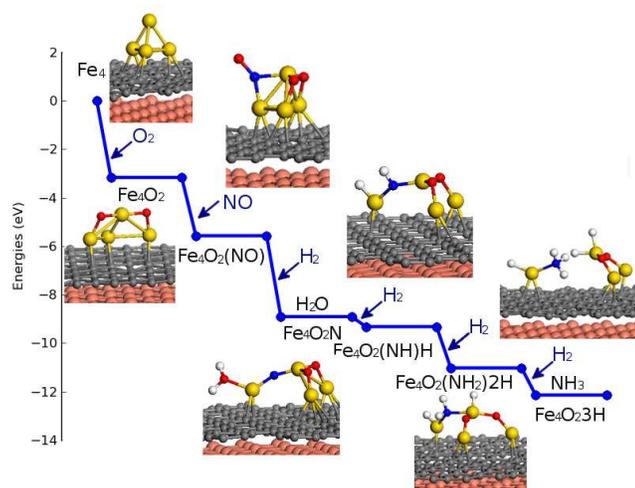
good agreement with previous work<sup>19</sup>. Oxidation of Fe<sub>4</sub> is performed where the approaching O<sub>2</sub> molecule is dissociated and adsorbed onto Fe<sub>4</sub> with -5.62 eV adsorption energy. The dissociated O atoms are adsorbed on the bridge site and top site of Fe atoms. Adsorption of NO forms Fe<sub>4</sub>O<sub>2</sub>NO with -3.17 eV of adsorption energy. The bond length of adsorbed NO is elongated from 1.16 Å, the bond length of gas phase NO, to 1.21 Å. The elongation of NO over Fe<sub>4</sub>O<sub>2</sub> is considered to be a critical step for the NO dissociation. Bader analysis indicates that electronic structures of NO over Fe<sub>4</sub>O<sub>2</sub> is changed compared to the gas phase NO. The bond type of gas phase NO is a polar covalent bond where O is positively charged by 0.4 electrons while N is negatively charged by 0.4 electrons. However, N is negatively charged by 0.6 electrons which are transferred from the Fe atoms while O is negatively charged by 0.4 electrons upon NO adsorption onto Fe<sub>4</sub>O<sub>2</sub>. Thus, both N and O are negatively charged resulting in the repulsion of N and O. The adsorption of H<sub>2</sub> molecule is then performed over Fe<sub>4</sub>O<sub>2</sub>NO where H<sub>2</sub> is dissociative and forms Fe<sub>4</sub>O<sub>2</sub>(NO)2H. Additional H<sub>2</sub> adsorption induces the formation of H<sub>2</sub>O and Fe<sub>4</sub>O<sub>2</sub>N2H. This is particularly interesting since the dissociation of NO upon H<sub>2</sub> adsorption occurs without activation barriers. The origin of the formation of H<sub>2</sub>O from NO and H<sub>2</sub>O without activation barriers is due to the contribution of charge state of NO. Upon the introduction of H<sub>2</sub> over Fe<sub>4</sub>O<sub>2</sub>(NO)2H, the O atom in NO is negatively charged by 1.2 electrons while N atom in NO is negatively charged by 0.8 electrons. Thus, both N and O in NO are negatively charged, resulting in the negative–negative repulsion towards dissociation of NO and the formation of H<sub>2</sub>O. Hence, undesirable NO is predicted to be dissociated and form H<sub>2</sub>O and N at low temperature.

The produced H<sub>2</sub>O could be a potential hydrogen source for the reaction through using electrolysis or re-visiting Fe<sub>4</sub>O<sub>2</sub> if a sufficient amount of water can be produced. In particular, calculations predict that one H atom is dissociated from H<sub>2</sub>O and form H and OH upon H<sub>2</sub>O adsorption onto Fe<sub>4</sub>O<sub>2</sub>. In that sense, hydrogen gas can be self re-supplied by using Fe<sub>4</sub>O<sub>2</sub>. At this stage, the formation of N<sub>2</sub>O is considered over Fe<sub>4</sub>O<sub>2</sub>N2H where the adsorption of NO over Fe<sub>4</sub>O<sub>2</sub>N2H leads to the formation of N<sub>2</sub>O without activation barriers. This indicates that N<sub>2</sub>O can be a possible by-product during the reaction. Further adsorption of H<sub>2</sub> on to Fe<sub>4</sub>O<sub>2</sub>N2H is also dissociative and forms Fe<sub>4</sub>O<sub>2</sub>(NH)3H. In this step, one of the dissociated H forms NH. Adsorption of another H<sub>2</sub> molecule is also dissociated over Fe<sub>4</sub>O<sub>2</sub>(NH)3H and both of the dissociated H atoms form a bond with N, resulting in the formation of NH<sub>3</sub>. It must be pointed out that the whole reaction is a barrier free process meaning that the reaction is active at low temperature. Thus, the formation of NH<sub>3</sub> from NO is achieved over Fe<sub>4</sub>O<sub>2</sub> at low temperature.

The barrier free NO conversion to NH<sub>3</sub> over gas phase Fe<sub>4</sub>O<sub>2</sub> is achieved. However, one has to confirm if the reaction in gas phase Fe<sub>4</sub>O<sub>2</sub> is also possible over supported Fe<sub>4</sub>O<sub>2</sub> clusters for practical applications. Graphene/Cu(111) is a proposed substrate that can preserve the structure and properties of Fe clusters<sup>14</sup>. Hence, Fe<sub>4</sub> is placed on graphene/Cu(111) substrate. The superlattice of graphene and Cu(111) is constructed where (4 × 4) supercell of Cu(111) and graphene consisting of 32 C atoms are constructed. The lattice mismatch is only 3.6%.

The ground state structure of Fe<sub>4</sub> on graphene/Cu(111) also has a pyramidal structure which is similar to one in gas phase Fe<sub>4</sub><sup>14</sup>. O<sub>2</sub> adsorption over Fe<sub>4</sub> on graphene/Cu(111) is performed where O<sub>2</sub> is dissociative over Fe<sub>4</sub>. However, O<sub>2</sub> adsorption energy is calculated to be -3.17 eV which is slightly lower than one found for gas phase Fe<sub>4</sub>. This is considered to be due to the charge transfer from Fe to graphene where Fe atoms over graphene/Cu(111) are positively charged by 0.6 electrons. Therefore, supported Fe atoms are less reactive than gas phase, resulting in low O<sub>2</sub> adsorption energies. NO is then adsorbed at the bridge site of Fe<sub>4</sub>O<sub>2</sub>. The bond length of adsorbed NO onto Fe<sub>4</sub>O<sub>2</sub> is elongated by 0.01 Å compared to the bond length of gas phase NO. The slight elongation of NO bond over Fe<sub>4</sub>O<sub>2</sub> is considered due to the negative–negative repulsion as N is negatively charged by 0.4 electrons while O is negatively charged by 0.2 electrons. H<sub>2</sub> adsorption over Fe<sub>4</sub>O<sub>2</sub>NO induces the formation of H<sub>2</sub>O, a different reaction step from gas phase Fe<sub>4</sub>O<sub>2</sub> where H<sub>2</sub> is adsorbed onto Fe<sub>4</sub>O<sub>2</sub>NO before the formation of H<sub>2</sub>O. One can expect that the electronic structure of Fe<sub>4</sub>O<sub>2</sub>NO is affected by the graphene/Cu(111) substrate, resulting in the direct formation of H<sub>2</sub> while the gas phase case requires extra H<sub>2</sub> adsorption to modify the electronic structure of gas phase Fe<sub>4</sub>O<sub>2</sub>NO. More

importantly, the conversion of NO to H<sub>2</sub>O is also observed for the supported cluster case. The origin of the barrier free conversion of NO to H<sub>2</sub>O and N rests on negative-negative repulsion of NO as seen in gas phase reaction. N is negatively charged by 0.8 electrons while O is negatively charged by 1.2 electrons upon the H<sub>2</sub> adsorption over Fe<sub>4</sub>O<sub>2</sub>NO. Additionally, in contrast to the gas phase case, the formation of N<sub>2</sub>O over supported Fe<sub>4</sub>O<sub>2</sub>N upon the adsorption of NO requires overcoming the activation barrier where the activation barrier is calculated to be 1.78 eV. Further H<sub>2</sub> adsorption is performed on Fe<sub>4</sub>O<sub>2</sub>N. H<sub>2</sub> adsorption on Fe<sub>4</sub>O<sub>2</sub>N is dissociative and one of the dissociated H adsorbed on Fe and another formed a N-H bond. Introducing another H<sub>2</sub> is also dissociative where one of the dissociated H atoms forms a Fe-H bond and another forms a N-H bond, resulting in NH<sub>2</sub>. Finally, additional H<sub>2</sub> adsorption is dissociative and forms NH<sub>3</sub> and Fe<sub>4</sub>O<sub>2</sub>3H shown in Figure 2. The reaction step for the conversion of NO to NH<sub>3</sub> between the gas phase and supported Fe<sub>4</sub>O<sub>2</sub> cases is slightly different. However, barrier free conversion of NO to NH<sub>3</sub> is still achieved over supported Fe<sub>4</sub>O<sub>2</sub>.



**Fig. 2** The reaction path of the conversion of NO to NH<sub>3</sub> over supported Fe<sub>4</sub> clusters on graphene Cu(111) with corresponding adsorption energies. Atomic color codes: Fe, yellow; O, red; N, blue; H, white; C, gray; Cu, reddish brown.

Barrier free ammonia production from NO over gas phase and supported Fe<sub>4</sub>O<sub>2</sub> clusters is proposed. If a sufficient amount of ammonia can be produced by the proposed reaction, undesirable nitric oxide can be converted to ammonia at low temperature. The reaction requires hydrogen gas which can be produced and recycled from the by-product H<sub>2</sub>O by using electrolysis or re-visiting Fe<sub>4</sub>O<sub>2</sub>. Thus, the production of ammonia can be operated at low temperature and a recyclable self-sustainable reaction could be achieved. In addition, barrier free NO conversion to ammonia is also observed over

Fe<sub>8</sub>O<sub>2</sub> and Fe<sub>12</sub>O<sub>2</sub> clusters. This suggests that a barrier free reaction over iron oxide clusters is generic and is predicted to occur for larger iron oxide clusters.

In conclusion, barrier free conversion of NO to NH<sub>3</sub> over Fe<sub>4</sub>O<sub>2</sub> is proposed. In particular, NO and H<sub>2</sub> over Fe<sub>4</sub>O<sub>2</sub> produce NH<sub>3</sub> and H<sub>2</sub>O. The whole reaction occurs without activation barriers, making it active at low temperature. The key reaction is barrier free NO conversion to N and H<sub>2</sub>O where negative-negative repulsion of NO over Fe<sub>4</sub>O<sub>2</sub> is considered to be a physical origin. Therefore, undesirable NO can potentially be used as a nitrogen source for ammonia production. The by-product H<sub>2</sub>O can be a potential hydrogen source by electrolysis or re-visiting Fe<sub>4</sub>O<sub>2</sub>, therefore, the reaction is self-sustainable. The conversion of NO to NH<sub>3</sub> over supported Fe<sub>4</sub>O<sub>2</sub> on graphene/Cu(111) is also investigated where the conversion also occurs without activation barriers. Thus, low temperature and environmentally friendly production of ammonia can be designed using iron oxide clusters.

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