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# Hydrogen spillover to oxygen vacancy of $TiO_{2-x}H_y/Fe$ : Breaking the scaling relationship of ammonia synthesis

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ABSTRACT. Optimizing kinetic barriers of ammonia synthesis to reduce the energy intensity has recently attracted significant research interest. The motivation for the research is to discover means by which activation barriers of N<sub>2</sub> dissociation and NH<sub>z</sub> (z = 1-2, surface intermediates) destabilization can be reduced simultaneously, i.e., breaking the "scaling relationship". However, by far only a single success has been reported in 2016 based on the discovery of a strong-weak N-bonding pair—transition metals (nitrides)-LiH. Described herein is a second example which is counter-intuitively founded upon a strong-strong N-bonding pair unveiled in a bifunctional nanoscale catalyst TiO<sub>2-x</sub>H<sub>y</sub>/Fe (where 0.02  $\leq x \leq 0.03$  and 0 < y < 0.03), in which hydrogen spillover (H) from Fe to cascade oxygen vacancies (O<sub>V</sub>-O<sub>V</sub>) results in the trapped form of O<sub>V</sub>-H on the TiO<sub>2-x</sub>H<sub>y</sub> component. The Fe component thus enables facile activation of N<sub>2</sub>, while the O<sub>V</sub>-H in TiO<sub>2-x</sub>H<sub>y</sub> hydrogenates the N or NH<sub>z</sub> to NH<sub>3</sub> easily.

# INTRODUCTION

The kinetic dilemma for the low-temperature Haber-Bosch ammonia synthesis originates from the "scaling relationship" of antagonistic activation energies between N<sub>2</sub> dissociation ( $E_{a(N-N)}$ ) and NH<sub>z</sub> intermediates (z = 0 to 2) destabilization;<sup>1-6</sup> catalysts that strongly activate N<sub>2</sub> also unfavorably hinder the transformation of NH<sub>z</sub> intermediates, and vice-versa.



**Scheme 1.** Breaking the "scaling-relation" in ammonia synthesis. (a) Schematic free-energy diagram for ammonia synthesis on strong (pink) and weak (blue) N-bonding catalysts. (b) The "scaling-relationship (S-R)" depicting  $E_{a(N-N)}$  and  $E_{a(NHz)}$  on the two sides of a seesaw: when one goes down, the other goes up. (c) Energy barrier engineering of dual active centers to break the "scaling-relationship" by using a strong N-bonding center for N<sub>2</sub> activation and a weak N-bonding center to destabilize NH<sub>z</sub> binding in previous design, while two strong N-bonding centers, Fe and O<sub>V</sub>-H of TiO<sub>2-x</sub>H<sub>v</sub>, are employed in this study.

Breaking this scaling relationship is key to improving the kinetics of ammonia synthesis and reaching the goal of less energy-intensive operating conditions.<sup>7-10</sup> Many theoretical investigations have attempted to understand how this scaling relationship could be broken,<sup>11-13</sup> and one study has claimed experimental success.<sup>14</sup> This experimental study exploited LiH in conjunction with strong N<sub>2</sub> reduction-capability Cr, Mn, Fe, Co, or Ni. In this reaction scheme, dissociated N atoms diffuse from the transition metals to LiH, forming LiNH<sub>z</sub>. The LiNH<sub>z</sub>

then reacts with  $H_2$  to regenerate LiH while producing  $NH_3$ . Easy  $N_2$  activation is achieved on strong N-bonding transition metals while  $NH_z$  destabilized easily on weak N-bonding LiH.

In contrast to this commonly accepted weak-strong N-bonding pair, we describe herein a counter-intuitive approach of both strong N-bonding elements breaking the scaling relationship based on our recently discovered highly-reactive photocatalyst  $TiO_{2-x}H_y/Fe$ .<sup>15</sup> In this hybrid catalyst, a Fe nanocrystal necklace (Fe-NL; bonding N strongly) is integrated with hydrogen-laden titanium oxide ( $TiO_{2-x}H_y$ ; also bonding N strongly) nanoparticles featuring in cascade oxygen vacancies ( $O_V-O_V$ ). During the catalytic process, easy N<sub>2</sub> dissociation and easy NH<sub>3</sub> assembly are triggered by Fe and hydrogen-laden oxygen vacancies (denoted  $O_V-H$ ; in  $TiO_{2-x}H_y$ ), respectively, while the  $O_V-H$  is recycled by a low-energy barrier hydrogen spillover from Fe via the cascade  $O_V-O_V$  pathway, thereby circumventing the kinetic dilemma, as illustrated in Scheme 1.

#### **RESULTS AND DISCUSSION**

**TiO<sub>2-x</sub>H<sub>y</sub>-promoted Ammonia Synthesis on Fe.** The thermocatalytic activity of ammonia synthesis was tested between 300 and 500 °C in a designed quartz plate reactor (Figure 1a, 1b). It should be noted that, to ensure a strict ambient pressure in the flow system, part of the syn gas (N<sub>2</sub> : H<sub>2</sub> = 1 : 3) was allowed to flow over the catalyst without reaction, which was a sacrifice to the measured rates in our reactor compared to the conventional micro-tube reactor (Figure S1). Therefore, to avoid misunderstanding on the reactivity of our catalysts, a benchmark commercial Fe catalyst<sup>16-18</sup> was used for reference. The pure Fe-NL prepared via solution-phase reduction (Figure S2) generated NH<sub>3</sub> concentrations between 14 and 82 ppm in the outlet gas, which increased with temperature. The industrial low-temperature benchmark of wüstite-based Fe catalysts demonstrated slightly higher NH<sub>3</sub> generation rates (18-92 ppm) than those of pure Fe-NL at lower temperatures while decreased to 69 ppm at 500 °C. Interestingly, by anchoring inactive TiO<sub>2-x</sub>H<sub>y</sub> nanoparticles to the Fe-NL (Figure S3 and S4), the measured NH<sub>3</sub> production rates increased to 110-560 ppm, approaching one order of magnitude higher than those of Fe-NL and the commercial low-temperature Fe catalyst. Different from the increased activity with temperature of Fe-NL, the TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL demonstrated a sharp activity decrease from 357 °C to 380 °C. Concurrently, its

apparent activation energy increased from 45 kJ/mol to 67 kJ/mol right after the activity decrease, and then back to 45 kJ/mol at higher temperatures. Given the apparent activation energy of Fe-NL was 61 kJ/mol, this result indicated a new active center in the  $TiO_{2-x}H_y$ /Fe-NL catalyst besides the commonly accepted Fe(0), possibly involving  $TiO_{2-x}H_y$  (Figure S5).

High-resolution X-ray photoelectron spectroscopy (XPS) analysis of the quenched TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL catalyst confirmed the Fe(0) active phase by demonstrating a mixed-valence surface of Fe(0)-to-Fe(III) and Ti(III)-Ti(IV) (Figure S6). N1s XPS spectra further strengthened the possibility of TiO<sub>2-x</sub>H<sub>y</sub> as the active center since the Ti-N<sup>3-</sup> species (398.4 eV) accompanies Fe-N<sup>3-</sup> (395.0 and 397.0 eV).<sup>15,19,20</sup> As the TiO<sub>2-x</sub>H<sub>y</sub> was incapable of N<sub>2</sub> activation according to the DFT calculation,<sup>15</sup> it may act as a center specific for the hydrogenation of atomic nitrogen. In this context, the reaction between N<sub>2</sub> and the deuterium-labelled TiO<sub>2-x</sub>D<sub>y</sub>/Fe-NL was examined and the ND<sub>3</sub> product was detected (Figure 1c), as monitored by <sup>2</sup>H-NMR of characteristic ND<sub>3</sub> triplet in the range of 6.6 to 7.2 ppm, while no ND<sub>3</sub> was produced when using control samples of TiO<sub>2-x</sub>D<sub>y</sub> or Fe-NL alone. This result agreed well with our previous in-situ diffuse reflectance spectroscopy result that TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL could react with N<sub>2</sub> producing NH<sub>3</sub> in a H<sub>2</sub>-free atmosphere,<sup>15</sup> suggesting that a working-in-tandem H-laden active center in TiO<sub>2-x</sub>H<sub>y</sub> could trigger N-hydrogenation to transcend that on pure Fe.



**Figure 1.** The strong N-bonding  $TiO_{2-x}H_y$  counter-intuitively promotes another strong N-bonding element Fe in ammonia synthesis. (a) Schematic of N<sub>2</sub> and H<sub>2</sub> activation on Fe and transfer to  $TiO_{2-x}H_y$  for NH<sub>3</sub> generation over  $TiO_{2-x}H_y$ /Fe catalyst. (b) Activity comparison of ammonia synthesis over  $TiO_{2-x}H_y$ /Fe-NL, pure Fe-NL and the commercial benchmark of wüstite-based Fe catalyst at 300 to 500 °C and 1 atm. (c) <sup>2</sup>H-NMR probe of ND<sub>3</sub> product after different samples reacting with N<sub>2</sub>. (d) Reported activation energy barrier of N<sub>2</sub> dissociation (E<sub>a(N-N)</sub>), as well as a volcano plot of turnover frequency (TOF) vs. E<sub>N</sub> in transition-metal-catalyzed ammonia synthesis. Blue and black data points from *Ref. 23*, adapted with permission from © 2015, Oxford University Press, and red data points from this work. How could an even stronger N-bonding  $TiO_{2-x}H_y$  (E<sub>N</sub> = -1.95 eV) promote the strong N-bonding Fe (E<sub>N</sub> =

1.59 eV) in ammonia synthesis? It is well-known that enhanced activity by far is only expected for a strong-weak N-bonding pair according to the scaling relationship, whereby a strong N-bonding element readily dissociates N<sub>2</sub> into atomic N via prominent  $\pi$  back-donation and then a weak N-bonding element enables easy NH<sub>z</sub> hydrogenation.<sup>21-24</sup> While the strong-strong N-bonding pair is projected to suffer from severe active sites blocking by strong N chemisorption which should not have broken the scaling relationship in theory.

**Oxygen Vacancies Trap Hydrogen, O<sub>V</sub>-H.** The first task in understanding ammonia synthesis on  $TiO_{2-x}H_y/Fe-$ NL was to identify the H-laden active sites in  $TiO_{2-x}H_y$ . This requires understanding the relationships between synthesis, structure and properties of  $TiO_{2-x}H_y$ . Consider the main solid-state chemical processes occurring in the synthesis of  $TiO_{2-x}H_y$ .<sup>25</sup>

$$(2x)\text{NaBH}_4 + \text{TiO}_2 \rightarrow \text{TiO}_{2-x}\text{H}_y + (x)\text{Na}_2\text{O} + (2x)\text{BH}_3 + (x - 0.5y)\text{H}_2$$
(Equation 1)

In this reaction, NaBH<sub>4</sub> serves to reduce Ti(IV) to Ti(III) with the concomitant formation of  $O_V$ . The challenge lies in understanding the structure and dynamics of the charge-balancing electrons and hydrogen atoms in TiO<sub>2</sub>. <sub>x</sub>H<sub>y</sub>; this could involve either localization upon or delocalization of electrons between titanium and oxygen vacancy sites (Figure 2a). Fortunately, EPR spectroscopy of TiO<sub>2-x</sub>H<sub>y</sub> as a function of stoichiometry (O<sub>V</sub> concentration, x) and temperature (T), in conjunction with deuterium isotope labelling TiO<sub>2-x</sub>D<sub>y</sub>, can help to resolve this dilemma.





**Figure 2.**  $O_V$ -H in TiO<sub>2-x</sub>H<sub>y</sub>. (a) Schematic of  $O_V$ -H formation in TiO<sub>2-x</sub>H<sub>y</sub>. (b-d) Oxygen vacancy concentrationdependent (b) and temperature-dependent EPR spectra for a low (c) and high (d) x value of TiO<sub>2-x</sub>H<sub>y</sub>. (e) Temperature-dependent EPR spectra of TiO<sub>2-x</sub>D<sub>y</sub> with low x value and inset is the enlarged spectra around g = 2.003. (f) High-resolution, spherical aberration-corrected TEM image of highly disordered TiO<sub>2-x</sub>H<sub>y</sub>, and possible element labelling for the selected area (yellow box). (g) The intensity ratio of EPR peaks, O<sub>V</sub>- and Ti(III)-related ones, measured at 106 K and 140 K for TiO<sub>2-x</sub>H<sub>y</sub> and TiO<sub>2-x</sub>D<sub>y</sub> samples, respectively. (h) Room-temperature EPR spectra of TiO<sub>2-x</sub>H<sub>y</sub> preheated at different temperatures in vacuum, and corresponding simulated EPR spectra of O<sub>V</sub>-*n*H with varied O<sub>V</sub>/H ratio.

The EPR spectra of TiO<sub>2-x</sub>H<sub>y</sub> sample with lowest O<sub>V</sub> concentration ( $x \le 0.001$ ) displayed typical axial line shapes for d<sup>1</sup> Ti(III) sites with slightly differing axial g-tensors ( $g_x = g_y \approx 1.975$ ,  $g_z \approx 1.940$ ), where the distortion from octahedral symmetry in TiO<sub>2</sub> likely originates from a combination of O<sub>V</sub> formation and/or Jahn–Teller effects, and an isotropic line shape with  $g \approx 2.003$  for a trapped electron on O<sub>V</sub> at 106 K.<sup>26-33</sup> Stoichiometrydependent EPR studies of TiO<sub>2-x</sub>H<sub>y</sub> samples, of which the preparation and quantification method of different x and y values will be discussed in detail later, further demonstrated the O<sub>V</sub> concentration-dependent nature of the two signals ( $1.92 \le g \le 1.99$  and  $g \approx 2.003$ ), as their peak intensities increased by ~40 times and ~17 times with the increased x values from  $\le 0.001$  to  $0.02 \le x \le 0.03$ , respectively. More interesting is the line shape of the triplet

at g  $\approx$  2.003 gradually evolved to a 9-line isotropic multiplet with increased line width, which was not present in TiO<sub>2</sub>, NaBH<sub>4</sub>, a grinded mixture of TiO<sub>2</sub>-NaBH<sub>4</sub> or TiO<sub>2-x</sub>-NaBH<sub>4</sub>, or any known doped-titanium oxides as far as we are concerned (Figure 2a and S7),<sup>31-40</sup> indicating an O<sub>V</sub>-related hyperfine splitting.

Temperature-dependent EPR studies of TiO<sub>2-x</sub>H<sub>v</sub> throw further light on the interpretation of these spectra. Increasing the temperature from 106 K to RT significantly decreased the Ti(III) line intensity relative to that of  $O_V$ -related multiplet for all Ti $O_{2-x}H_v$  samples (Figure 2b-2d and S8), which indicated the dynamic exchange process involving electrons transfer from Ti(III) to O<sub>V</sub>-related sites and finally being localized. With capabilities of balancing the highly localized charge and easy access to O<sub>V</sub>, the hydrogen atom was thus suspected as the origin of the EPR multiplet via O<sub>V</sub>-H coupling. To testify this idea, a quantitative EPR analysis of the temperature dependence was conducted for  $TiO_{2-x}H_v$  and  $TiO_{2-x}D_v$  samples. In theory, if the electron transfer involving H/D on the  $O_V$  sites, Ti(III) $\rightarrow$ Ov-H/D, a kinetic isotope effect would be expected. Consistently, when the H nucleus was replaced by D nucleus (x  $\leq$  0.01), the Ti(III) peak intensities of TiO<sub>2-x</sub>D<sub>y</sub> decreased sharply with temperature (4.35 for 106 K/140 K) compared to that of  $TiO_{2-x}H_v$  (1.95 and 2.45 of highest and lowest x values for 106 K/140 K), while the Ov-related peak intensity (g = 2.003) remained at 106, 140 and 195 K for  $TiO_{2-x}D_{y}$  but kept decreasing with temperature for TiO<sub>2-x</sub>H<sub>v</sub> (Figure 2g and S8). Furthermore, the triplet of TiO<sub>2-x</sub>D<sub>y</sub> and TiO<sub>2-x</sub>H<sub>y</sub> (x  $\leq$  0.001) around g  $\approx$  2.003 at 140 K was similar but differed significantly at higher temperature such as 220 K and RT, the former collapsed to isotropic O<sub>V</sub> while the latter maintained the triplet (Figure 2c and 2e). These kinetic isotope effect conspired the Ov-H coupling in TiO<sub>2-x</sub>H<sub>v</sub> and thus the EPR multiplet could be assigned as OV-*n*H following the "2nl + 1" rule (*l* represents the nuclear spin of H or D while *n* represents their numbers).<sup>33,41</sup> The premise for such an  $O_V$ -*n*H coupling was the close proximity of a distribution of  $O_V$  and H in Ti $O_{2-x}H_V$ , which was supported by the highly defective nature of  $TiO_{2-x}H_{y}$  as shown in the high-resolution double spherical aberration corrected transmission electron microscopy (TEM) image (Figure 2f) where the formation of vicinal  $O_V$  was possible both on the surface and in the bulk.

Typically, the O<sub>V</sub> or H ion (or polyhydride) is highly reactive,<sup>42-66</sup> thus providing an ideal opportunity to

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double check the assignment of  $O_V$ -H via the H-O<sub>V</sub> decoupling. In theory, the 9-line multiplet would degrade back to conventional O<sub>V</sub> without localized hydrogens. Therefore, the EPR spectra of TiO<sub>2-x</sub>H<sub>v</sub> (0.02  $\leq$  x  $\leq$  0.03, 0 < v < 0.03) sample with gradually released hydrogen were recorded, which was realized by dividing a single sample into eight portions and subjecting to vacuum at 200 °C, 300 °C, 350 °C, 375 °C, 400 °C, 425 °C, 450 °C and 500 °C, respectively (Figure 2h). To summarize, from room temperature (RT) to 300 °C, there was no obvious 1<del>6</del> 16 changes to the isotropic multiplet in  $TiO_{2-x}H_{y}$ . In the range 330-375 °C, the intensity of the isotropic multiplet 18 started to increase, especially the inner most two peaks. Then a significant transformation of the isotropic multiplet into an anisotropic signal was observed in the range 400 to 450 °C with the concurrent appearance of additional 2g Ti(III) signal. At 500 °C only the pure O<sub>V</sub> EPR signal remained, with an increased intensity and a narrower line 25 width. These results confirmed the H and O<sub>V</sub> dependence of the EPR multiplet, which was further supported by the EPR simulations of OV-*n*H coupling with a constant  $a_{\rm H} = 7.7$  Gauss. Further detailed discussions were also **₽**₽ made to exclude other possibilities in the multiplet assignment (Supporting Information). On the other hand, the ₽1 13 32 result indicated that the O<sub>V</sub>-H sites in TiO<sub>2-x</sub>H<sub>v</sub> began to dissociate to O<sub>V</sub> and atomic H or H<sub>2</sub> above 300 °C to 14 54 possibly participate in the ammonia synthesis, which continues to completion by 500 °C. An intermediate step appears to involve  $Ti^{4+}-O_V-\bullet H \rightarrow Ti^{3+}-O_V + H/H_2$ . **B**5 **Coupled Fe and Ov-H Hydrogen Cycle.** As suggested by EPR measurements that both Fe and Ov-H are active

in ammonia synthesis in the initial TiO<sub>2-x</sub>H<sub>v</sub>/Fe-NL catalyst, the following steps are proposed for the ammonia synthesis process where \* indicates an adsorbed state:

$Fe + 0.5N_2 \rightarrow Fe - 0.5*N_2 \rightarrow Fe - *N$	(Equation 2)
$Fe + 0.5H_2 \rightarrow Fe - 0.5*H_2 \rightarrow Fe - *H$	(Equation 3)
$Fe-*N + 3(Fe-*H) \rightarrow 4Fe + NH_3$	(Equation 4)
$O_V$ -H + *N (from Fe to $O_V$ ) $\rightarrow O_V$ -*NH	(Equation 5)
$O_V$ -NH + 2*H (from Fe to $O_V$ ) $\rightarrow O_V$ -*NH <sub>3</sub> $\rightarrow O_V$ + NH <sub>3</sub>	(Equation 6)

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$$O_V + *H \text{ (from Fe or } O_V) \rightarrow O_V -H$$
 (Equation 7)

Among these processes, Equations 2 through 4 are known to generate ammonia on Fe surfaces via the Langmuir-Hinshelwood mechanism.<sup>5</sup> The nitrogen-hydrogenation enabled by  $O_V$ -H, Equations 5 and 6, are unique to Ti $O_2$ -<sub>x</sub>H<sub>y</sub>/Fe, being made a complete catalytic cycle by insertion of hydrogen into  $O_V$  sites in Equations 7, which is also the key step to confirm  $O_V$ -H as the catalytic center in Ti $O_{2-x}$ H<sub>v</sub>.



**Figure 3.** Hydrogen spillover from Fe to  $O_V$ -H. (a) Schematic reduction process of  $TiO_{2-x}H_y/Fe-NL$ , as well as hydrogen transfer during H<sub>2</sub>-TPR measurement. (b) H<sub>2</sub>-TPR-TCD spectra of Fe-NL, titanium oxides of  $TiO_{2-x}H_y$  and  $TiO_2$ , hybrid catalysts of  $TiO_{2-x}H_y/Fe-NL$  and  $TiO_2$  /Fe-NL, and the commercial Fe catalyst. (c) H<sub>2</sub>-TPR-MS spectra of  $TiO_{2-x}H_y/Fe-NL$  with H<sub>2</sub> and H<sub>2</sub>O products being monitored. (d) Comparison of H<sub>2</sub>-TPR-TCD spectra for  $TiO_{2-x}H_y/Fe-NL$  before and after partial hydrogen release, which is realized via pre-heating at 400 °C *in situ*. (e) H transfer from Fe to  $O_V$ -D to produce HD over  $TiO_{2-x}D_y/Fe-NL$ .

To experimentally examine whether the hydrogen transfer via Equations 7 in  $TiO_{2-x}H_y/Fe-NL$ , temperature-programmed reduction (TPR) measurements were performed in a H<sub>2</sub> atmosphere (Figure 3a). TiO<sub>2</sub>, Fe-NL, TiO<sub>2</sub>/Fe-NL and commercial Fe control samples were found to consume H<sub>2</sub> during temperature ramping. By contrast, the H<sub>2</sub>-TPR-TCD measurements of TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL demonstrated unusual negative peaks suggesting net gas release (Figure 3b),<sup>67,68</sup> which was further confirmed as H<sub>2</sub> by MS (Figure 3c). 1 2 3<sup>1</sup>

4 52

6 73

8 9<sub>4</sub> 10

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Upon partially dissociating the O<sub>V</sub>-H through heating the TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL sample to higher temperatures (from 330 °C to 400 °C; 2O<sub>V</sub>-H  $\rightarrow$  2O<sub>V</sub> + H<sub>2</sub>) before TPR measurements, the hydrogen release decreased at higher temperatures (above 320 °C), as expected, but surprisingly increased at lower temperatures (100 to 320 °C). Together with the result that the H<sub>2</sub> release peak of TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL centered at a lower temperature than that of pure TiO<sub>2-x</sub>H<sub>y</sub>, this increased H<sub>2</sub> gas release at low temperature suggested an additional O<sub>V</sub>-H destabilization pathway possibly involving hydrogen spillover (O<sub>V</sub>-H + \*H<sub>spillover</sub>  $\rightarrow$  O<sub>V</sub> + H<sub>2</sub>) besides the hydrogen coupling of two O<sub>V</sub>-H in TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL (Figure 3b and 3d). This result could correlate well with the interesting temperaturedependent ammonia synthesis rates of TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL, i.e., hydrogen spillover could either promote NH<sub>3</sub> generation via O<sub>V</sub>-H cycling at < 357 °C and > 380 °C, or impede N<sub>spillover</sub> + O<sub>V</sub>-H = O<sub>V</sub>-NH if its speed is too high to reduce the O<sub>V</sub>-H concentration (H<sub>spillover</sub> + O<sub>V</sub>-H = H<sub>2</sub> + O<sub>V</sub>) from 357 °C to 380 °C (Figure 2b and S9). The D labelled TPP MS results for TiO<sub>2</sub>. D (Fe NL further demonstrated that HD was the major product

The D-labelled TPR-MS results for TiO<sub>2-x</sub>D<sub>y</sub>/Fe-NL further demonstrated that HD was the major product during ramping, which confirmed that the 2O<sub>V</sub>-D = 2O<sub>V</sub> + D<sub>2</sub> reaction was overwhelmed by O<sub>V</sub>-D + \*H<sub>spillover</sub> =  $O_V$  + HD (Figure 3e). Based on the above results, it was concluded that the Fe-H bond dissociation and H spillover to O<sub>V</sub>-H proceeded at much lower temperature than the O<sub>V</sub>-H coupling reaction, which is consistent with the fact that H<sub>2</sub> quickly desorbs from Fe-H above 200 °C (the measured Fe-H bond energy is only 60-65 kcal/mol).<sup>69</sup> Note that the coupling of \*D to \*H or \*D is random on pure metal surfaces;<sup>48</sup> hence, a highly selective generation of HD rather than a HD-D<sub>2</sub> mixture could not proceed on an unmodified Fe surface, thus excluding the possibility of reverse H-spillover from O<sub>V</sub>-D to Fe. This result is very interesting when compared to the advanced oxyhydride BaTiO<sub>3-x</sub>H<sub>x</sub> supported transition metal catalysts,<sup>47,53,70,71</sup> where electron and hydrogen exchanges are observed in both catalysts while the direction for the hydrogen transfer is opposite (Figure S6d and S6e), demonstrating the high flexibility and potential in tuning ammonia synthesis activity via different H-laden oxides.

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**Figure 4.** Hydrogen spillover for H replenishment. (a) H<sub>2</sub>-TPR-TCD spectra of  $TiO_{2-x}H_y/Fe-NL$  and  $TiO_{2-x}H_y$  in five "heating and cooling" runs. (b) Standard stability test of  $TiO_{2-x}H_y/Fe-NL$  for ammonia synthesis at 405 °C, 10 atm, and GHSV: 36,000 h<sup>-1</sup>. Inset: picture of extruded catalyst, 40-mesh. (c) Calibration plot for  $O_V$  quantification using TEMPO (2, 2, 6, 6-tetramethylpiperidine-1-oxyl radical) and Mn(II) as standard and reference, respectively, obtained by double integration of the signals, and (d) corresponding EPR spectra of 20 mg TiO<sub>2-x</sub>H<sub>y</sub> after heating to 500 °C in a H<sub>2</sub> atmosphere.

Five consecutive H<sub>2</sub>-TPR measurements in a row was used to probe the reversibility of the  $O_V \leftrightarrow O_V$ -H process in TiO<sub>2-x</sub>H<sub>y</sub>/Fe. These results indicated that TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL could continuously release H<sub>2</sub> via an O<sub>V</sub>-H + \*H<sub>spillover</sub>  $\rightarrow O_V$  + H<sub>2</sub> process. Most of the H<sub>2</sub> was evolved in the first run, owing to a high initial hydrogen population at the O<sub>V</sub> sites of as-prepared TiO<sub>2-x</sub>H<sub>y</sub>. A lesser amount of H<sub>2</sub> was evolved in the second run, and yields stabilized in the third through fifth runs (Figure 4a). This suggested that the O<sub>V</sub>-H destabilization and Fe hydrogen spillover-induced O<sub>V</sub>-H regeneration could reach a dynamic equilibrium state in the presence of H<sub>2</sub>. This hypothesis is supported by the enduring on-stream stability of TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL during ammonia synthesis within 20 h (Figure 4b).

A TiO<sub>2-x</sub>H<sub>y</sub> control sample demonstrated continuous H<sub>2</sub> release over five H<sub>2</sub>-TPR runs, suggesting hydrogen activation could also proceed on pure O<sub>V</sub> or O<sub>V</sub>-H. The quantity of H<sub>2</sub> released per Ti atom in TiO<sub>2</sub>.  $_xH_y$ /Fe-NL was ~3.7 times that of pure TiO<sub>2-x</sub>H<sub>y</sub>, suggesting hydrogen spillover from Fe, rather than O<sub>V</sub> H<sub>2</sub> activation, is the major pathway for hydrogen replenishment at O<sub>V</sub>-H sites. The concentration of unpaired electrons at O<sub>V</sub> sites of TiO<sub>2-x</sub>H<sub>y</sub> (after heated at 500 °C in H<sub>2</sub>) was ~2.6 x 10<sup>21</sup> per mole of TiO<sub>2-x</sub>H<sub>y</sub> and the

values were  $0.02 \le x \le 0.03$  and y < 0.03 for TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL during reaction at 500 °C (Figure 4c, 4d, S10 and S11). This estimate was obtained using the equilibrium concentration of O<sub>V</sub>-H via H<sub>2</sub>-TPR and the x and y values of TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL were 0.03 and < 0.03 for "Ti-•O<sub>V</sub>-H-Ti" or 0.02 and < 0.02 for "Ti-•O<sub>V</sub>•-H-Ti", where • denotes a localized electron (Supporting Information). Based on this result, the TOF vs. O<sub>V</sub> was estimated to be as high as  $1.0 \times 10^{-2}$  s<sup>-1</sup> at 405 °C under 10 atm.



**Figure 5.** Hydrogen spillover to  $O_V$  breaks the "scaling relation" in ammonia synthesis. (a) The DFT model of TiO<sub>2-x</sub>H<sub>y</sub>/Fe and schematic ammonia synthesis cycle, and (b) corresponding free energy diagram and (c) overall energy barriers. **Theoretic interpretation of Fe-O<sub>V</sub>-H breaking the "scaling relationship".** Spin-polarized DFT calculation was then utilized for N<sub>2</sub>/H<sub>2</sub> reactions over O<sub>V</sub>-H and Fe two active centers in TiO<sub>2-x</sub>H<sub>y</sub>/Fe. A Fe(111) facet was chosen due to its surface C<sub>7</sub> sites which are believed to be the catalytic center for nitrogen dissociation over iron.<sup>72-75</sup> The TiO<sub>2-x</sub>H<sub>y</sub> model was then placed on this Fe(111) surface after abstracting one *z*-axial oxygen atom of a TiO<sub>6</sub> octahedral unit, in accordance with previous studies.<sup>76,77</sup> An O<sub>V</sub>-H site was crafted by abstracting two vicinal oxygen atoms (forming two vicinal O<sub>V</sub>), followed by refilling one O<sub>V</sub> site with a hydrogen atom lying in the *xy*-plane (Figure 5a, S12 and S13). This vicinal O<sub>V</sub>-O<sub>V</sub>-H site in TiO<sub>2-x</sub>H<sub>y</sub> makes spillover favorable in ammonia

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synthesis, as will be amplified in the following section.

The N binding energy and activation energy of N<sub>2</sub> dissociation were computed over the C<sub>7</sub> site of the Fe(111) surface and on the O<sub>V</sub>-H site of TiO<sub>2-x</sub>H<sub>v</sub>. It was found that the Fe(111) C<sub>7</sub> site both strongly bound and readily dissociated N<sub>2</sub> ( $E_N = -1.51$  eV and  $E_{a(N-N)} = 1.03$  eV, Steps III to IV in Figure 5b). While the O<sub>V</sub>-H site bound N even more strongly ( $E_N = -2.09 \text{ eV}$ ; Figure S14), it suffered from a difficult N<sub>2</sub> dissociation step ( $E_{a(N-N)}$ ) = 2.73 eV) consistent with the inactivity of  $TiO_{2-x}H_v$  in ammonia synthesis. Upon N<sub>2</sub> dissociation on Fe, \*N migrated to  $O_V$ -H of Ti $O_{2-x}H_v$  with an associated  $E_a = 1.23$  eV. Next, NH spontaneously formed upon reaction with  $O_V$ -H, with a small  $E_a = 0.26 \text{ eV}$  (Steps IV' to VII in Figure 5b, also see Figure S15 and Supplementary Videos S1 and S2). Subsequent NH<sub>3</sub> assembly via  $O_V$ -NH + \*H<sub>spillover</sub>  $\rightarrow O_V$ -NH<sub>2</sub> and  $O_V$ -NH<sub>2</sub> + H<sub>spillover</sub> =  $O_V$ -NH<sub>3</sub> bore E<sub>a</sub> values of 1.42 eV and 1.28 eV, respectively (Steps VI to XI in Figure 5b). The partial density of states analyses indicated that these accessible E<sub>a</sub>s for H<sub>2</sub> and NH<sub>x</sub> were associated with activation capability of  $O_V$  and Ti(III) (Figure S16). After NH<sub>3</sub> was generated, it readily desorbed from the TiO<sub>2-x</sub>H<sub>y</sub> surface at temperatures above 100 °C,<sup>69</sup> as also revealed by the NH<sub>3</sub>-TPD spectra (Figure S17). With a calculated desorption energy of 1.56 eV, this easy NH<sub>3</sub> desorption may be a result of energy compensation from the exothermic hydrogen adsorption and activation.<sup>78</sup> Then dissociated hydrogen atoms, mainly from hydrogen spillover and partly from O<sub>V</sub>-H<sub>2</sub> dissociation, refilled the O<sub>V</sub> forming O<sub>V</sub>-H to close catalytic cycle (step XII to XIV; Figure 5b and S18). Based on the results of this calculation, the unique behavior of  $O_V$ -H is revealed: it bonds N stronger than Fe but cannot dissociate N<sub>2</sub>, only able to accept spillover N/H, while free from the difficult NH<sub>x</sub> hydrogenation at the same time, a novel observation for active centers in ammonia synthesis.

Theoretically possible competing mechanisms were also examined to further support this "spillover to  $O_V$ " one. NH<sub>3</sub> generation on TiO<sub>2-x</sub>H<sub>y</sub> via the hydrogen spillover pathway (E<sub>a</sub> = 1.42 eV) was confirmed to be more favorable than reverse hydrogen spillover triggered NH<sub>3</sub> assembly on Fe (E<sub>a</sub> = 2.53 eV; Figure 5c, S20). Side reactions such as nitrogen filling O<sub>V</sub> to form O<sub>V</sub>-N did not influence the catalytic cycle, as it was easily hydrogenated to O<sub>V</sub>-NH with an E<sub>a</sub> of 0.96 eV via hydrogen spillover (Step XII to XV' of Figure 5b). These

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results specifically define hydrogen spillover from Fe to O<sub>V</sub> as a key step in ammonia synthesis on TiO<sub>2-x</sub>H<sub>y</sub>.

The reaction orders of N<sub>2</sub> were 0.29 for TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL and 0.51 for Fe-NL (Figure S21), suggesting that the surfaces of both catalysts are almost saturated with N<sub>2</sub> or atomic N, leading to very weak dependences of the reaction rates on gas-phase N<sub>2</sub>. DFT results demonstrated the N<sub>2</sub> activation barrier on Fe was increased by TiO<sub>2</sub>. <sub>x</sub>H<sub>y</sub> loading (0.05 eV vs. 1.03 eV), the lower reaction order of TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL might originate from the increased N/N<sub>2</sub> adsorption on the surface TiO<sub>2-x</sub>H<sub>y</sub> and more accessible surface Fe(0) sites due to the favorable spillover of atomic N to TiO<sub>2-x</sub>H<sub>y</sub>. The reaction order of NH<sub>3</sub> for TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL (-0.87) was more negative than that of Fe-NL (-0.45), which is very common in ammonia synthesis when a transition metal is promoted by other components. Meanwhile, the reaction orders of H<sub>2</sub> were 1.36 and 0.79 for TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL and Fe-NL, respectively, indicating the additional hydrogen demand of TiO<sub>2-x</sub>H<sub>y</sub>/Fe-NL possibly for N<sub>spillover</sub> + O<sub>V</sub>-H = O<sub>V</sub>-NH, which involves a hydrogen spillover related O<sub>V</sub>-H recycle.

The easy hydrogen spillover to  $O_V$  sites should originate from the unique  $O_V$ -(H) structure of TiO<sub>2-x</sub>H<sub>y</sub>. DFT calculations indicated that the surface cascade "O<sub>V</sub>-O<sub>V</sub>" structures enabled a low E<sub>a</sub> from 0.42 eV to 0.84 eV for hydrogen transfer. In contrast, hydrogen transfer via surface lattice oxygen ("O<sub>V</sub>-O-O<sub>V</sub>") exhibited a much higher E<sub>a</sub> = 2.58 eV (Figure 6a and 6b). Furthermore, another possible cascade "surface O<sub>V</sub>-bulk O<sub>V</sub>" was also proved feasible for hydrogen transfer, with activation energy barriers of 0.48 eV and 0.95 eV for H storage while 1.20 eV and 0.39 eV for H release (Figure S22). This result could explain the reversible hydrogen storage behavior of TiO<sub>2-x</sub>H<sub>y</sub>, which also agreed with recent observation that hydrogen could transfer in certain depth inside a metal oxide.<sup>79</sup> The cascade "O<sub>V</sub>-O<sub>V</sub>" assembled from O<sub>V</sub>-(H) monomers, which could maximize the distance of hydrogen transfer on the TiO<sub>2-x</sub>H<sub>y</sub> surface (Figure 6c), was experimentally supported by the TEM image of TiO<sub>2-x</sub>H<sub>y</sub> with highly O-deficient sites and the hyperfine splitting of OV-*n*H (Figure 2g and 2h).





**Figure 6.** Low-energy-barrier hydrogen spillover pathway engendered by " $O_V-O_V$ " cascade. (a) Schematic activation energy diagram and, (b) structure of hydrogen transfer through cascade " $O_V-O_V$ " (left) and O-obstructed  $O_V-O_V$  (right) pathways. The structures and activation energy barriers were obtained using DFT. (c) Schematic of cascade " $O_V-O_V$ " pathway via the  $O_V$ -(H) monomers on the surface of TiO<sub>2-x</sub>H<sub>y</sub>, facilitating hydrogen transfer.

#### CONCLUSION

Facile N<sub>2</sub> and H<sub>2</sub> dissociation on a nano Fe and subsequent hydrogenation of N by spillover H in oxygen vacancies  $(O_V-H)$  on TiO<sub>2-x</sub>H<sub>y</sub> in a bifunctional TiO<sub>2-x</sub>H<sub>y</sub>/Fe catalyst together enable the "scaling relation" in ammonia synthesis to be broken. As both Fe and TiO<sub>2-x</sub>H<sub>y</sub> are strong N-bonding components, the ability of TiO<sub>2-x</sub>H<sub>y</sub>/Fe to overcome the "scaling relationship" represents a paradigm shift in ammonia synthesis.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Methods, Figure S1-S22, Supplementary Videos 1 and 2, and additional references

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#### Notes

The authors declare no competing interests.

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