Tailoring widely used ammonia synthesis catalysts for H and N poisoning resistance†

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Despite many advancements, an inexpensive ammonia synthesis catalyst free from hydrogen and nitrogen poisoning, and capable of synthesizing ammonia under mild conditions is still unknown and is long sought-after. Here we present an active nanoalloy catalyst, RuFe, formed by alloying highly active Ru and inexpensive Fe, capable of activating both N2 and H2 without blocking the surface active sites and thereby overcoming the major hurdle faced by the current best performing pure metal catalysts. This novel RuFe nanoalloy catalyst operates under milder conditions than the conventional Fe catalyst and is less expensive than the so far best performing Ru-based catalysts providing additional advantages. Most importantly, by integrating theory and experiments, we identified the underlying mechanisms responsible for lower surface poisoning of this catalyst, which will provide directions for fabricating poison-free efficient NH3 synthesis catalysts in future.

Introduction

Ammonia (NH3) is a strategic chemical produced in large quantities, most of which is used as a fertilizer to support food production. Currently, NH3 is synthesized through the Haber–Bosch process operated at 400–600 °C and 20–40 MPa and using an Fe catalyst, along with H2 produced from steam reformation of hydrocarbons. This process contributes around one-third to the overall greenhouse gas emissions, challenging many researchers to work towards finding an alternative, sustainable and efficient NH3 synthesis catalyst. Among many catalysts, Ru-based catalysts have attracted a lot of attention as they can synthesise NH3 efficiently under milder conditions compared to the conventional Fe catalyst used in the Haber–Bosch process currently. However, despite the excellent catalytic activity, Ru-based catalysts have attracted a lot of attention as they can synthesise NH3 efficiently under milder conditions compared to the conventional Fe catalyst used in the Haber–Bosch process currently. However, despite the excellent catalytic activity, Ru-based catalysts get easily deactivated due to H-poisoning of the catalyst surface, suppressing the industrialization of Ru catalysts for mass production of NH3. Some very recent Ru-based catalysts include Ru/C12A7e−, where C12A7e− works as an excellent electron donor and a reversible hydrogen-storage material, and Ru/Pr2O3 which contains low-crystalline Ru nano-layers formed by reaction between Ru and strongly basic Pr2O3. In these catalysts the synergistic interaction between Ru and its support reduces the deterioration of the catalyst due to H-poisoning and accelerates the cleavage of the N≡N bond of N2 thereby reducing the barrier for the rate-determining step of the NH3 synthesis reaction.

For the enhancement of the durability of ammonia synthesis catalysts, in this work we choose a simple strategy where we alloyed a high performance Ru catalyst that interacts weakly with N, with inexpensive Fe catalyst that interacts strongly with N, to design a rational NH3 synthesis catalyst with distinct properties. This strategy is simple yet very difficult to execute due to the large difference in the oxidation–reduction potentials of Ru and Fe ions, i.e., 0.455 V for Ru/Ru2+ and −0.447 V for Fe/Fe2+, making it impossible until now to chemically reduce Ru and Fe to solid solution type Ru–Fe alloys containing more than 50 at% Fe. In this work, we demonstrate the synthesis of a well-mixed Ru–Fe nanoalloy supported on MgO (Ru–Fe/MgO) by using a modified thermal decomposition method. The newly synthesized Ru–Fe/MgO catalyst with 50% contribution from each Ru and Fe (denoted as RuFe) exhibits a higher H2 production efficiency and lower poisoning than both pure Ru and Fe catalysts as long as we compare the catalytic performances without promoters and focus only on the intrinsic activities of the catalyst. The underlying mechanisms explaining the origin of higher performance and lower poisoning of the RuFe nanoalloy catalyst is discussed in the following sections.

Results and discussion

We prepared Ru–Fe/MgO catalysts by hydrogen reduction of precipitates produced on MgO supports via thermal decomposition of impregnated carbonyl complexes of Ru and Fe ions.

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(for details see ESI†). In this method, metal compositions were controllable by changing the mixing ratio of metal complexes (Table S1, ESI†). Both MgO supported Ru and Fe nanoparticle catalysts (Ru/MgO and Fe/MgO, respectively) were prepared in a similar way. X-ray diffraction measurements suggested that metallic phases are formed on all prepared catalysts (Fig. S1, ESI†).

Scanning electron microscopy (STEM) images of Ru/MgO, RuFe/MgO and Fe/MgO are shown in Fig. 1a–c, respectively (see also Fig. S2, ESI†). On these three catalysts, we can see that the nanoparticles are well dispersed on MgO supports. The average diameters of the Ru, RuFe and Fe particles on MgO were calculated to be $6.2 \pm 2.1$, $19 \pm 5.7$ and $58 \pm 9.2 \text{ nm}$, respectively, i.e., nanoparticles formed on Ru–Fe/MgO catalysts have diameters between those of Ru and Fe nanoparticles (Table S2, ESI†). We performed energy dispersive X-ray (EDX) measurements to clarify the distribution of Ru and Fe atoms in the nanoparticle (Fig. 1d–f and Fig. S3, ESI†). In Fig. 1d and e, Ru and Fe ions, which are shown in red and green, respectively, seem to be uniformly distributed, resulting in mostly yellowish nanoparticles originating from the overlap of red-colored Ru and green-colored Fe (Fig. 1f). X-ray photoelectron spectroscopy measurements for catalysts reduced under flowing H₂ clarified that Fe/MgO cannot promote the NH₃ synthesis reaction whereas we could not observe any products on Fe/MgO, suggesting that the alloying effect on the performance was pronounced at higher pressures and temperatures where influence from the surface poisoning becomes conspicuous. We further conducted catalytic reactions by changing the partial pressure of reaction gases, N₂ and H₂, or the product gas, NH₃, and calculated the reaction order for each gas. We applied an equation for NH₃ synthesis to a general formula of the reaction kinetics and found the reaction order $\alpha$ (or $\beta$) with $N_2$ (or $H_2$) on Ru/MgO and RuFe/MgO. Fig. 3a and b show the amount of NH₃ produced while changing the partial pressure of $N_2$ or $H_2$ on Ru/MgO and Ru–Fe/MgO, respectively. The reaction orders for $N_2$ on Ru/MgO and RuFe/MgO below 0.1 (1.0) MPa of the reaction pressure were calculated to be 1.4 (0.89) and 0.97 (0.81), respectively, which implies that a higher pressure of $N_2$ accelerates catalytic reactions both on Ru/MgO and RuFe/MgO. However, the corresponding reaction order on Ru/MgO for $H_2$ was $-0.14$ ($-0.48$), suggesting that the Ru catalyst is relatively easily poisoned on alloy catalysts is not achievable at present due to their different adsorption conditions and adsorption energies for CO or $H_2$. Thus, we normalized the catalytic performance using the surface area of catalysts, which were calculated from average diameters of the particles in STEM images. At 0.1 MPa, TOFs on Ru/MgO and RuFe/MgO below 400 °C seemed almost the same, i.e., $3.0 \times 10^{16}$ and $4.1 \times 10^{16}$ NH₃ molecule m⁻² s⁻¹, respectively. Meanwhile, at 500 °C, RuFe/MgO showed twice the performance on Ru/MgO, i.e., TOFs on Ru/MgO and RuFe/MgO were $8.1 \times 10^{16}$ and $1.9 \times 10^{17}$ NH₃ molecule m⁻² s⁻¹, respectively. Furthermore, at 1 MPa and 600 °C, RuFe/MgO showed three times higher performance compared to that on Ru/MgO, suggesting that the alloying effect on the performance was pronounced at higher pressures and temperatures where influence from the surface poisoning becomes conspicuous.

Next, we synthesized NH₃ using the prepared catalysts in the temperature range from 300 to 600 °C at 0.1, 0.5 and 1 MPa. The catalytic performances at 400 °C for Ru–Fe/MgO with various compositions of Ru and Fe are presented in Fig. S5 (ESI†). Surprisingly, among all the prepared catalysts, RuFe/MgO exhibited the highest catalytic performance at 0.5 and 1 MPa whereas we could not observe any products on Fe/MgO, suggesting that Fe/MgO cannot promote the NH₃ synthesis reaction under the conditions applied here. Temperature dependences of the turnover frequency (TOF) for NH₃ synthesis on Ru/MgO and RuFe/MgO are provided in Fig. 2. As mentioned above, the particle sizes of the three catalysts are considerably different and simultaneous evaluation of active surface areas of Ru and Fe...
with H₂ gas under higher pressures. In contrast, the order on RuFe/MgO for H₂ is 0.50 (0.71), suggesting that the poisoning from H₂ is suppressed on RuFe/MgO and higher pressures of H₂ exhibit a positive influence on NH₃ synthesis, which contributes to the increase in TOF on RuFe/MgO [Fig. 2].

To identify the origin of the low surface poisoning and high catalytic performance on a RuFe alloy catalyst in contrast to Ru and Fe metal catalysts, we conducted an in-depth theoretical calculation for the NH₃ production reaction on both Ru and RuFe catalysts using density functional theory (DFT). Since the RuFe alloy and Ru consist of an hcp structure,¹⁰ we used the Ru hcp structure to model the Ru and the alloy catalysts. For preparing the Ru catalyst, we considered the (0001) surface of Ru (Fig. 4a) as it is typically the lowest surface energy plane of Ru and hence the most abundant surface on most particles. For modelling the alloy surface, we replaced 50% of Ru atoms with Fe atoms (Fig. 4b) as experimentally the highest catalytic activity is obtained for the alloy having 50 at% of both Ru and hence the most abundant surface on most particles. For Ru (Fig. 4a) as it is typically the lowest surface energy plane of Ru, RuFe catalysts using density functional theory (DFT). Since the RuFe alloy and Ru consist of an hcp structure,¹⁰ we used the Ru hcp structure to model the Ru and the alloy catalysts. For preparing the Ru catalyst, we considered the (0001) surface of Ru (Fig. 4a) as it is typically the lowest surface energy plane of Ru and hence the most abundant surface on most particles. For modelling the alloy surface, we replaced 50% of Ru atoms with Fe atoms (Fig. 4b) as experimentally the highest catalytic activity is obtained for the alloy having 50 at% of both Ru and Fe atoms (Fig. S3, ESI†). The adsorbates are placed on the top layer of the slab at the various adsorption sites. Throughout this work, the plane-wave-pseudopotential approach was utilized,¹¹–¹⁷ details of which are given in the ESI.†

Since the TOF for NH₃ production depends on the binding energy of the reactants, intermediates and products to the active site, first we investigated the active sites for N₂, N, H, H₂, NH, NH₂ and NH₃ by calculating the adsorption energies and preferred geometries of both Ru and RuFe catalyst surfaces. As shown in Fig. 4a, there are four adsorption sites on Ru: top of Ru (T), the bridge between two Ru atoms (B), the three-fold hcp hollow (H) and the threefold fcc hollow (F). The most stable adsorption sites for N₂, N, H, NH, NH₂ and NH₃ are T, H, F, H, B and T, respectively. These most stable sites on the Ru surface found in the calculations are in good agreement with the suggested sites in the literature.¹⁸–²³ The distance of N from the Ru surface was found to be 1.05 ± 0.05 Å experimentally,²⁰ which also agrees well with our calculations (Table S4, ESI†). As expected, both NH₂ and N₂ prefer to bind to the T site of the Ru surface due to the electrostatic interaction between the electron-rich N atom having a lone pair and the most electron-deficient site on the surface. While in pure Ru only a few non-equivalent absorption sites can be found, the presence of Fe atoms in the RuFe alloy leads to several possible adsorption sites at: (1) top of Ru (T-Ru), (2) top of Fe (T-Fe), (3) Ru–Ru–Fe hcp (H-Ru3Fe), (4) Fe–Fe–Ru hcp (H-Fe3Ru), (5) Ru–Fe–Fe fcc (F-Ru2Fe), (6) Fe–Fe–Ru fcc (F-Fe2Ru), (7) Ru–Ru bridge (B-RuRu), (8) Ru–Fe bridge (B-RuFe) and (9) Fe–Fe bridge (B-FeFe) (Fig. 4b). The most stable adsorption sites for N₂, N, H, NH, NH₂ and NH₃ adsorption on the RuFe alloy surface were found to be T-Ru, H-Fe3Ru, F-Ru2Fe, F-Fe2Ru, B-RuFe and T-Ru, respectively. The adsorption energies and geometries of the most favorable adsorption sites for the intermediates of NH₃ synthesis reaction on Ru and RuFe surfaces are summarized in Tables S4 and S5 (ESI†), respectively. As alloying expands the lattice which in-turn reduces the deformation cost of the lattice due to the introduction of adsorbates, the RuFe surface showed a slightly higher binding energy with the adsorbates (except NH₃) compared to the Ru surface.

To analyze the surface activity of the alloy surface compared to the Ru surface, we conducted spin-density calculations (Fig. S6, ESI†) which revealed that alloying leads to unpaired spin on the Fe atoms. Fe-induced spin polarization can be understood from the variation in the Fe–Ru bond length and the variation in the Fe atomic charge. The variation in the bond length between atoms of the alloy results in the reduction of the covalent bond strength and enhancement in the ionic bonding interaction, thus giving rise to the accumulation of unpaired electrons making the RuFe surface more active than the Ru surface. This analysis is also in accordance with the results obtained from the Bader charge calculations,²⁴ which showed that approximately 0.3 electrons from Fe shift to Ru in the RuFe alloy. This is not an unexpected result as the electronegativity of Ru (2.3) is higher than that of Fe (1.83). We further confirmed the charge transfer direction by conducting work function calculations (Fig. S7, ESI†) which showed that the Fe surface has lower (3.45 eV) work function compared to the Ru surface (4.57 eV) rationalizing the electron transfer from Fe to Ru when two metals are mixed together. In addition, the RuFe surface showed a work function (4.23 eV) higher than the Fe surface and lower than the Ru surface, as expected.

To further explain the comparatively higher activity of the alloy surface we present in Fig. S8 (ESI†) the partial density of states (PDOS) projected on the d-orbital of Ru, RuFe and Fe catalysts, along with their calculated spin up and spin down d-band centers (vertical line). Clearly, the d-band of RuFe shifted upwards compared to the d-band of Ru and shifted downwards compared to the d-band of the Fe. The five-fold degenerate d-states of the alloy catalyst (Fig. S9, ESI†) revealed that the three-fold degenerate t₂g (dₓz, dᵧz, and dₓz) states are more responsible than the 2-fold degenerate e_g (dₓ²−y² and dₓz) states for the narrower d-band near the d-band center. This appropriately tuned the d-band of the alloy catalyst making it highly active for NH₃ production and helped in reducing the hydrogen and nitrogen poisoning of the alloy catalyst in contrast to Ru and Fe catalysts, respectively, which get poisoned easily with H and N species, respectively.

To analyze (H,N)-poisoning of the Ru, RuFe and Fe catalysts, we further analyzed the H-catalyst and N-catalyst interactions...
by calculating the d-PDOS of the surface atomic layer of Ru, RuFe and Fe catalysts with and without adsorbates (H, N). Fig. 5 indicates that the d-band structure changes significantly upon H adsorption on all the three catalysts. However, this change in d-states due to overlap with H s states, which represents the strength of H-catalyst interaction, is maximum for the Ru catalyst and is reduced for the RuFe catalyst explaining the H-resistivity of the RuFe catalyst compared to the Ru catalyst, observed in experiments. Furthermore, on comparing the filled and the empty d states of the three catalysts with those of N p states, we found that only Fe is capable of donating electrons to the empty N orbitals due to its appropriate Fermi level ($E_f$) (Fig. 6).

leading to strong Fe–N interaction and thus higher N-poisoning of the Fe catalyst as compared to Ru and RuFe catalysts. The Fermi level on RuFe is located at a slightly lower energy but is the nearest among three, implying that the RuFe catalyst is capable to efficiently activate N$_2$ without severe N-poisoning.

We calculated the barrier for N adsorption on Ru, Fe and RuFe surfaces to quantify the activity of the RuFe surface as compared to Ru and Fe catalysts (Fig. S10, ESI†). The energies are shown as a function of the relative number of Ru neighbors in the active site, denoted by $z$. The most stable adsorption site for N is the top of Ru for both Ru and RuFe surfaces. For the Fe surface, we chose the geometry of N/Fe shown in Fig. S11 (ESI†), as this geometry was reported to be the most stable one for N adsorption on the Fe catalyst. For the RuFe surface $z$ corresponds to a value of (Ru/(Ru + Fe)) 0.71 as it has 5 Ru and 2 Fe neighbors in the first and the second atomic layers. For Ru and Fe surfaces, $z$ is 1 and 0, respectively. Clearly, as expected, the interaction energy between a N adsorbate and the RuFe surface is intermediate between that of the constituents and a distribution of bond energies will exist for a given distribution of sites on the RuFe catalyst.

There are several indications in the literature that electrochemical catalysts, molecular catalysts and naturally occurring nitrogenase enzymes reduce N$_2$ via associative adsorption (or hydrogenation of N$_2$), rather than dissociative adsorption (where N$_2$ molecules are first dissociated followed by subsequent addition of hydrogen). Therefore, next we investigated the overall reaction energetics for NH$_3$ synthesis on both Ru and RuFe surfaces by analyzing the associative mechanism in which only H$_2$ molecules dissociate and NH$_3$ is formed by adding hydrogen atoms to the N$_2$ molecule (Fig. 7) for both surfaces. First, an NH$_3$ molecule is formed after the addition of five H atoms, followed by the formation of the second NH$_3$ molecule after addition of the sixth hydrogen. Fig. 7 shows that the stable N$_2$H$_2$ and N$_2$H$_3$ intermediates on the Ru surface become unstable on the RuFe surface along with unstable N$_3$H$_2$ and N$_2$H$_4$ intermediates and the overall reaction is exothermic on both surfaces. Further, formation of N$_2$H seems to be the rate-limiting step on Ru (as also reported in ref. 26) and RuFe surfaces. However, on the RuFe surface the barrier to form N$_2$H...
Conflicts of interest

There are no conflicts to declare.

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Notes and references