



A mini-review on the role of quasi-compounds in catalysis — The ammonia synthesis reaction on metals

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ABSTRACT

Catalysis is generally explained by the reaction of adsorbed species, but in certain cases it can be also understood by the involvement of surface “quasi-compounds”. A quasi-compound is a combination of elements that can exist only on a specific crystalline surface, but cannot be taken out from the surface. A prominent example is found in the ammonia synthesis reaction. Decomposition of NH_3 occurs on most metals and its kinetics is governed by the rate-determining desorption of N_2 , but the synthesis reaction occurs only on a limited number of clean metals. Precious metals in pure form are inactive for the ammonia synthesis reaction, however, the reaction of adsorbed $\text{N}(\text{a})$ with H_2 on precious metals gives NH_3 via $\text{NH}(\text{a})$. Among base metals Ni is also inactive for the ammonia synthesis reaction. But N-atoms form a quasi-compound Ni_3N on Ni(110) rather than adsorbed species, and the hydrogenation of Ni_3N with H gives NH_3 via the $\text{NH}(\text{a})$ intermediate. On the other hand, adsorption of NH_3 gives only $\text{NH}_2(\text{a})$ on these metals. Interestingly, Ni_3N on Ni(110) becomes inactive for reaction with H-atoms at temperatures higher than approximately 500 K, because the quasi-compound Ni_3NH undergoes decomposition to Ni_3N at approximately 500 K; that is, no $\text{NH}_2(\text{a})$ is formed at temperatures higher than 500 K. A large inverse hydrogen isotope effect ($r_{\text{D}}/r_{\text{H}} = 2\text{--}3$) has been reported for the ammonia synthesis reaction on a doubly promoted Fe-catalyst, and interpreted on thermodynamic grounds. Therefore, we propose an alternative explanation for this inverse isotope effect based on the fact that the reaction of $\text{N}(\text{a})$ on the precious metals with $\text{H}_2 + \text{D}_2$ ($\text{H}_2/\text{D}_2 = 1$) gives equal amounts of $\text{NH}(\text{a})$ and $\text{ND}(\text{a})$. As discussed in this review, the contribution of labile quasi-compounds, $[\text{Fe}_x\text{N}]$ and $[\text{Fe}_x\text{NH}]$, is useful in this regard, and accounts for the formation of NH_3 by the hydrogenation of an NH_2 intermediate formed from $[\text{Fe}_x\text{NH}]$. According to this mechanism, the activity of the Fe-surface is given by the steady rate of formation of labile $[\text{Fe}_x\text{N}]$ and $[\text{Fe}_x\text{NH}]$ to give adsorbed $\text{NH}_2(\text{a})$ on the Fe-surface.

1. Introduction

The interaction of surfaces with external species leads to many types of structures including ordered adatoms [1], supported clusters [2,3], subsurface defects [4], reconstructed patterned structures [5,6], two-dimensional alloys [7], and inverse layers [5] as documented by Hrbek [1], Rodriguez and co-workers [7]. Among these are also surface quasi-compounds as suggested by Tanaka [8]. The definition of materials is different in chemistry and in physics. If a compound behaves differently in some chemical reactions, it is accepted as a novel material in

chemistry, which is essentially different from the definition of materials in physics, which concentrates on structural properties. When the chemical properties of surfaces are considered, the known chemical properties are not those of the parent materials but those of their exposed surfaces, as illustrated below (Scheme 1).

For instance, the atoms exposed when a solid is fractured, or graphene is cut, or a polymer is cleaved will have different properties from those of the original materials. The specific arrangement of atoms obtained by such processes can be obtained in principle by theoretical calculations, but it is difficult to anticipate the reactivity of the surfaces.

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When metal surfaces are exposed to N_2 , O_2 or H_2 , unusual species that are different from the adsorbed molecules or atoms are formed on some crystal planes, and these entities were named “quasi-molecules” or “quasi-compounds” by Tanaka [8]. It should be recognized that the term surface compound has been used in the past. The term was introduced in 1962 by Sachtler and van Raijen [9], to describe chemisorption complexes. These were deemed to be compounds in their own right because they resulted in “demetallization” of the substrate, namely a decrease in the magnetic and/or electronic nature of the underlying metal. In the early days of infrared spectroscopy applied to surfaces, Eischens noted the correspondence between surface compounds and conventional compounds [10]. In the studies of alloys, Sachtler and van der Plank suggested that the formation of surface compounds by chemisorption implied that catalysis was not a collective phenomenon, but highly localized [11]. In an early broad review of organometallic compounds, Ugo drew analogies between bonding in complexes and the electronic nature of chemisorbed species [12]. A study of oxygen adsorption on a well-ordered K/Ru(001) surface by Hrbek [2] demonstrated the formation of a stable potassium-oxygen surface complex of stoichiometry close K_2O_2 . Thus, there is ample precedent for the quasi-compounds suggested by Tanaka. These quasi-compounds are essentially different from adsorbed atoms on the surface, because they have their own stoichiometry and conformation depending on the crystal plane. In contrast adsorbed species are considered not to drastically change the structure of the surface and to have variable stoichiometry. The quasi compounds cannot be taken out from the surface as a compound, that is, these compounds can exist only in a specific two-dimensional space. The formation of the quasi-compounds may be explained by total energy calculations, but the chemical properties of these new materials are difficult to predict by first principles calculations.

In considering quasi-compounds on metals, what Germer [13] wrote in Physics Today in 1964 is profound, because no one had considered quasi-compounds at that time.

“Nickel-atoms on a (110) face are completely rearranged at room temperature by the adsorption of half a monolayer of H-atoms; yet hydrogen is held exceedingly weakly upon this surface. Rarely, in the still somewhat limited experience of these experiments, does adsorption of any foreign atom upon any crystal surface occur without the accompanying drastic rearrangement of the atoms of the metal or semiconductor surface. This reconstruction of surfaces by adsorption of foreign atoms upon them is without doubt much the most significant result that has been obtained up to this time from low-energy electron-diffraction studies. It will have a profound influence upon basic ideas regarding chemical reactions which go on upon surfaces. Although it is new, it should not be too surprising, for rearrangement of surface metal atoms is obviously required when oxidation takes place.”

2. Adsorption and the formation of quasi-compounds on metals

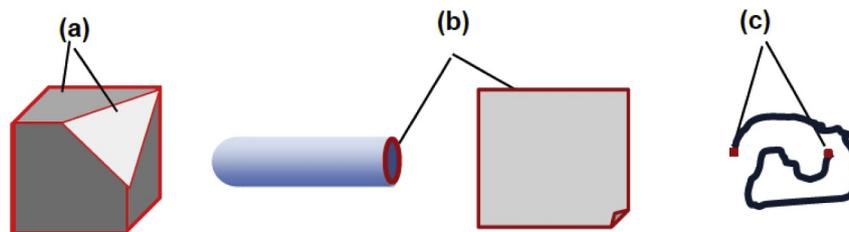
When a Cu(100) surface is exposed to O_2 at room temperature, adsorbed O(a) atoms form nano-size $c(2 \times 2)$ -O domains, as shown in Fig. 1(b) [14,15]. The boundaries of the nano-size $c(2 \times 2)$ -O domains

fluctuate with time, which proves that adsorbed O(a) atoms move on the surface, but the $c(2 \times 2)$ -O domains do not grow into large-size domains at room temperature. This phenomenon is essentially different from the growth of $(-CuO-)$ strings along the $\langle 001 \rangle$ direction on the Cu(110) surface, shown in Fig. 1(c). In this respect, the Cu(110) and Cu(100) planes form different species in the presence of O_2 . These $(-CuO-)$ strings play a key role in catalysis, but so far the reconstruction of Cu(110) by O_2 has been explained as a surface-structure sensitive reaction.

The ammonia synthesis reaction on single crystal Fe surfaces is a well-studied system. Ammonia synthesis rates over iron catalysts have been reported to be changed drastically during some period of synthesis reaction. Somorjai and co-workers [16,17] have demonstrated this using single crystal iron catalysts. They found that the activity of Fe(111) was approximately 415 times higher than that of Fe(110), but all crystal surfaces took on almost equally high catalytic activity to that of Fe(111) after deposition of 2 ML of Al_2O_3 and treatment with H_2O at 723 K. Before their works, Ozaki and co-workers [18] found this phenomenon over pure iron powder catalyst and showed the results in the experimental section. Later, Amariglio and Rambeau [19] studied the phenomena over industrial iron catalyst in detail and suggested the special active site only occurring during the steady synthesis reaction. Boudart and co-workers [20] considered a previous suggestion that Fe atoms with a specific trigonal conformation on Fe(111) called C_7 -sites are responsible for the catalysis, and considered that Al_2O_3 allowed reconstruction of the inactive faces to form C_7 -sites. According to this idea, they explained the activation of other crystal planes by the formation of C_7 -like sites. As discussed below, an alternative to adsorption may be the formation of labile quasi-compounds (Fe_xN) in the presence of Al_2O_3 .

Adsorption or the formation of quasi-compounds can be clearly exemplified by the adsorption of H-atoms upon Ni surfaces. As shown by Klienle et al. [21], the LEED pattern of the Ni(110) surface changes from $p(1 \times 1)$ to $p(2 \times 1)$ when the coverage of H(a) exceeds $\theta_H = 1.0$ at 220 K, and the change of the pattern is reversible depending on the coverage of adsorbed H(a) at this low temperature, as shown in Fig. 2(a). That is, the reversible change is caused by adsorbed H(a) atoms on the Ni(110) surface. However, an entirely different phenomenon was observed by Besenbacher et al [22] at room temperature, as shown in Fig. 2(b). As shown by model (i) and model (ii) in Fig. 2(b), the array of Ni atoms on the Ni(110) surface undergoes a reversible change at low temperature on adsorption of H(a), but the reaction of H(a) with Ni atoms on the Ni(110) surface at room temperature leads to irreversible formation of a quasi-compound $(-NiH-)$. The growth of $(-NiH-)$ strings in model (ii) represent reversible and irreversible changes of the Ni(110) surface caused by H_2 depending on temperature. The Ni(110) surface and their $(-NiH-)$ array along the $\langle 110 \rangle$ direction is similar to the growth of $(-NiO-)$ strings along the $\langle 001 \rangle$ direction on the Ni(110) surface.

As shown in Fig. 3(a), the (3×1) array of $(-NiO-)$ strings is compressed to a (2×1) array with increasing density of $(-NiO-)$ strings on the Ni(110) surface. Although the heat of adsorption of O_2 is several times larger than that of H_2 , Sprunger et al. [23] observed an interesting compression of $(-NiO-)$ strings from a (3×1) to $p(2 \times 1)$ array



Scheme 1. Materials with dimensionality lowered by one are formed by cleaving parent materials as shown (a), (b), and (c).

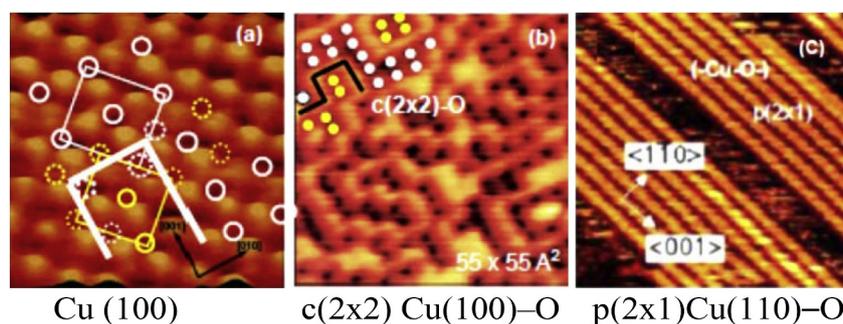


Fig. 1. (a) STM image of a clean Cu(100) surface. Circles show two different phases of $c(2 \times 2)O(a)$ domains, (b) Adsorption of O(a) in nano-size $c(2 \times 2)-O$ domains with different phases [14], and (c) Self-assembled array of $(-Cu-O-)$ strings in a $p(2 \times 1)$ structure on a Cu(110) surface [15].

on a $p(3 \times 1)Ni(110)-O$ surface on exposure to H_2 at room temperature, as shown in Fig. 3(b).

It should be pointed out once again that the $(-NiH-)$ and $(-Ni-O-)$ strings coexist, but very few adsorbed O(a) and H(a) are present on the same crystal planes, which is like a phase change as a function of pressure in three-dimensional space at a given temperature taking place in this two-dimensional potential space. Taking these facts into account, one should consider the dynamic cooperation of adsorbed species and quasi-compounds, as described below.

The existence of unconfirmed compounds on the surface was

suggested to occur in “pestle chemistry”, and this method was developed recently as a ball-milling method to prepare some new active catalysts. Formation of a highly active catalyst (FeN_x/C) by ball-milling carbon with phenanthroline and ferrous acetate, which provides a surface material exhibiting comparable activity to that of Pt/C catalysts for the reduction of oxygen, is a practical example [24,25]. It was also reported that highly dispersed N_4Fe in a graphene matrix prepared by this method catalyzed the oxidation of benzene to phenol [26]. However, care should be taken in trying to explain such phenomena via traditional mechanisms using conjectured models involving average

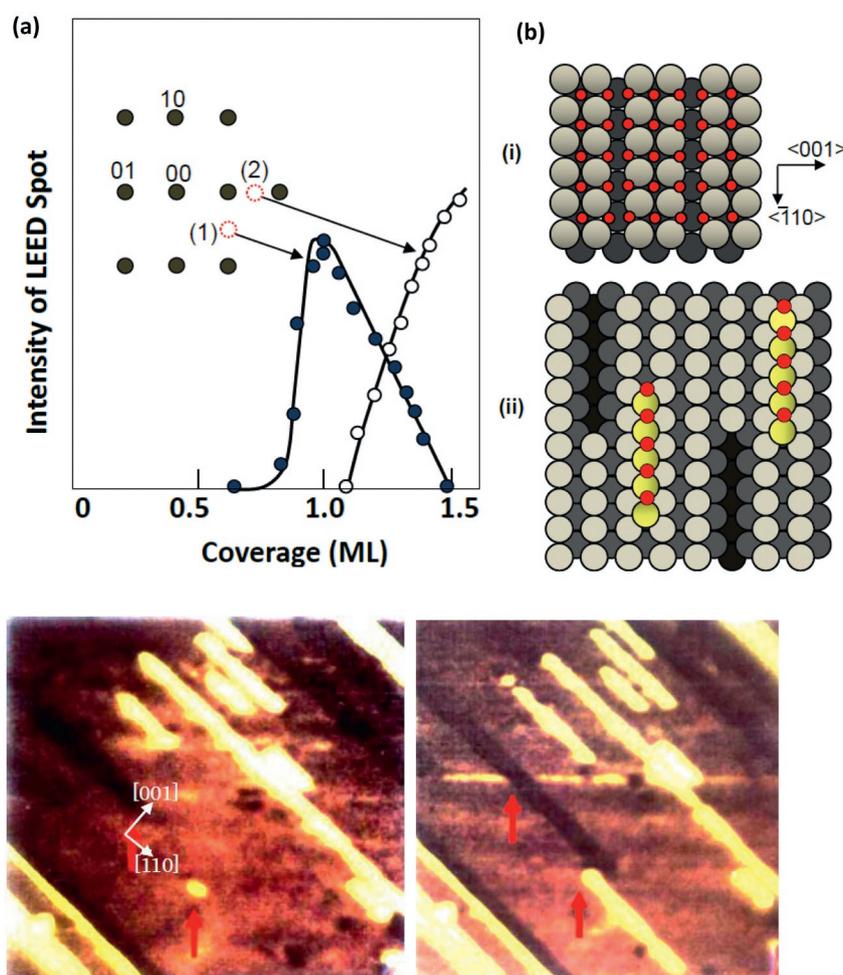


Fig. 2. (a) Reversible change of the LEED pattern of Ni(110) surface caused by the adsorption of H(a) at 220 K. The $p(2 \times 1)$ spot (red open circle-(1)) has maximum intensity at $\theta_H = 1.0$. When the coverage exceeds $\theta_H = 1.0$, new spots of a $p(1 \times 2)$ pattern appear (red open circle-(2)), and the intensity is maximized at $\theta_H = 1.5$ [21]; (b) Irreversible growth of $(-NiH-)$ strings on a Ni(110) surface along the $\langle 110 \rangle$ direction (red arrows) on exposure to H_2 at room temperature [22]. Model (i) and model (ii) represent reversible and irreversible changes of the Ni(110) surface caused by H_2 depending on temperature.

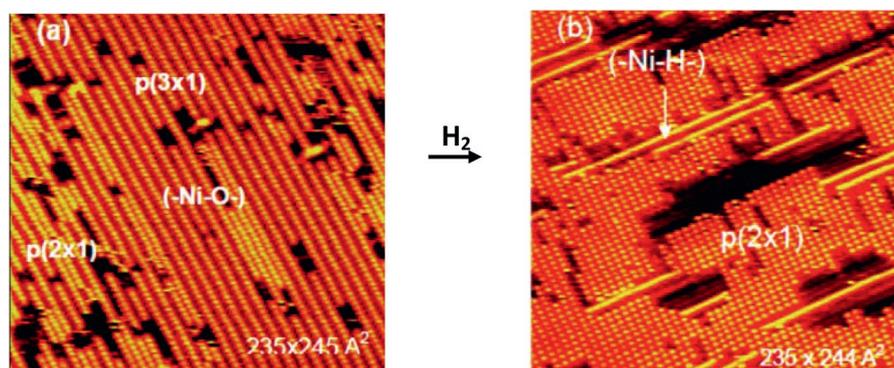


Fig. 3. The (3×1) array of $(-Ni-O-)$ strings is compressed to a (2×1) array on a $Ni(110)-O$ surface at room temperature by the growth of $(-Ni-H-)$ strings in the $< 1-10 >$ direction [23].

distances attained from EXAFS measurements [27].

The ammonia synthesis reaction is an important chemical reaction taking place in the presence of suitable catalysts and in most cases the kinetics is explained by the rate-determining dissociation of N_2 . Recently, a shift in the rate-determining step has been reported on a high activity Ru catalyst supported on a Ca aluminate electride support [28]. The reverse ammonia decomposition has been studied by many investigators, partly to understand the synthesis reaction and the decomposition kinetics were well explained by the rate-determining desorption of N_2 on most metals. However, a difficult question has remained, “why does the decomposition of NH_3 occur on many metals, while the synthesis of NH_3 happens on only a few metals?” For example, hydrogenation of adsorbed N(a) atoms on precious metals (Pd, Rh, and Pt) as well as Ni_3N on $Ni(110)$ forms NH_3 , but these metals are inactive for ammonia synthesis by the reaction of N_2 with H_2 . The paradox of this reversible chemical reaction can be explained by the existence of labile quasi-compounds of metals with nitrogen, as discussed in this review. It should be stressed that the discussions in this review pertain to pure noble metals without promotion. Aika and Ozaki found that promotion of precious metals with potassium activates them for ammonia synthesis [29,30].

If N(a)-adsorbed $c(2 \times 2)$ Pd(100), Rh(100) and Pt-Rh(100) surfaces are exposed to hydrogen, formation of NH(a) is detectable by various spectroscopic methods, and the amount of N(a) is lowered by formation of NH_3 [31]. An equilibration of $N(a) + H \rightleftharpoons NH(a)$ on these metals was also confirmed at 400 K, but the intensity of NH(a) and ND(a) peaks observed for the reaction with $H_2 + D_2$ ($H_2/D_2 = 1$) showed no appreciable hydrogen isotope effect [31,32]. The amount of N(a) on the metals was decreased by hydrogenation, $NH(a) + H_2 \rightarrow NH_3$, but no detectable amount of $NH_2(a)$ was observed during the hydrogenation of N(a) and NH(a) on the metals [31].

Takehiro et al. [33] prepared a $p(2 \times 3)$ $Ni(110)-N$ surface completely covered with Ni_3N (Auger intensity ratio of $N/Ni = 0.25$) by performing the chemical reaction $NO + H_2 \rightarrow N(a) + H_2O$ on $Ni(110)$ in an excess of H_2 ($H_2/NO = 150/1$) at 650 K. The $p(2 \times 3)$ $Ni(110)-N$ surface is inactive for the dissociation of H_2 , so that the surface is passive toward reaction with H_2 . The Ni_3N on $p(2 \times 3)$ $Ni(110)$ surface reacts with H atoms prepared by dissociation of H_2 on a hot W filament (2.0×10^{-6} Torr), and the formation of NH(a) was confirmed by observation of an electron energy loss peak of N-H(a) at about 3260 cm^{-1} (N-D at 2410 cm^{-1}), and the formation of Ni_3NH at the terminal end of Ni_3N rows on the $p(2 \times 3)$ $Ni(110)-N$ surface was suggested by STM [34]. The quantity of N-atoms decreased with time by reaction with H atoms, but the rate of decrease of N-atoms was temperature independent up to 500 K, as shown in Fig. 4(b), where the rate of decrease of N atoms was given by the flux of H atoms. It should be pointed out that the intensity of the energy loss peak of NH(a) was lowered as the temperature rose and disappeared at 550 K, as shown in Fig. 4(a). That is, a dynamic equilibrium of $Ni_3N + H \rightleftharpoons Ni_xNH$ is established on the p

(2×3) $Ni(110)-N$ surface during the hydrogenation of Ni_3N with H atoms at temperatures lower than 550 K [33]. Adsorbed $NH_2(a)$ on the Ni surface, formed by hydrogenation of the quasi-compound Ni_xNH , is very quickly hydrogenated to NH_3 . There is a very similar example for the hydrogenation of carbidic carbon on $Ni(100)$ [35], where the hydrogenation of CH_3 to CH_4 readily occurs under lower temperature. If the temperature is raised higher than 550 K, the $p(2 \times 3)$ $Ni(110)-N$ surface becomes passive to H-atoms, as shown in Fig. 4(b). That is, the quasi-compound Ni_3NH decomposes to Ni_3N at temperatures higher than 500–550 K, so that no $NH_2(a)$ formation takes place on the Ni-surface. This result proves that if dissociation of N_2 and the formation of Ni_3N would occur at temperatures higher than 550 K, the Ni surface has no ability to support the ammonia synthesis reaction. The result in Fig. 4(b) suggests a new idea for the “dynamic protection” of a surface from high temperature H atoms, that is, if a reactor surface is covered with $p(2 \times 3)$ $Ni(110)-N$, no quasi-compound Ni_xNH would be formed if the temperature is kept at 530–800 K, which may be applicable to reactor walls for the T-D nuclear-fusion reaction [33].

On the other hand, a large inverse hydrogen isotope effect of $r_D/r_H = 2-3$ was reported by Ozaki et al. [36] in the ammonia synthesis reaction on a doubly-promoted $K_2O/Al_2O_3/Fe$ catalyst, and this inverse hydrogen isotope effect was explained by the retardation of the dissociation of N_2 by adsorbed NH(a) or ND(a), that is, $NH(a) > ND(a)$. An alternative explanation for this inverse hydrogen isotope effect on the ammonia synthesis reaction involves the hydrogenation of the labile quasi-compounds Fe_xN and Fe_xNH . This is discussed in Section 3, which analyzes the ammonia synthesis reaction on Fe catalysts.

3. Contribution of quasi-compounds to the ammonia synthesis reaction

The ammonia (NH_3) synthesis reaction is a historic catalytic reaction developed to produce nitrogenous fertilizers and explosives. Currently, NH_3 has been proposed as a hydrogen carrier, because H_2 is readily obtained by the decomposition reaction without the formation of greenhouse gases. The synthesis reaction occurs only on a limited number of clean metals [29]; the poor catalytic activity of precious metals (excluding Ru) mainly lies in the strong “poisoning” effect of adsorbed H which blocks active site from N_2 activation. However, decomposition of NH_3 occurs on most metals and its kinetics is governed by the rate-determining desorption of N_2 [37]. The decomposition reaction of NH_3 has been studied by many investigators on various metals in the last 100 years, and for many metals the kinetics of the decomposition of NH_3 appears to follow the rate-determining desorption of N_2 , as shown in Fig. 5 [37], where the kinetics depends on a parameter ($-\Delta H_0$) related to the heat of adsorption of molecules.

For a reaction at steady-state the free energy change (ΔG), or driving force of the reaction, is given by the balance of the forward and backward reaction rates, and the free energy drop for each step is given

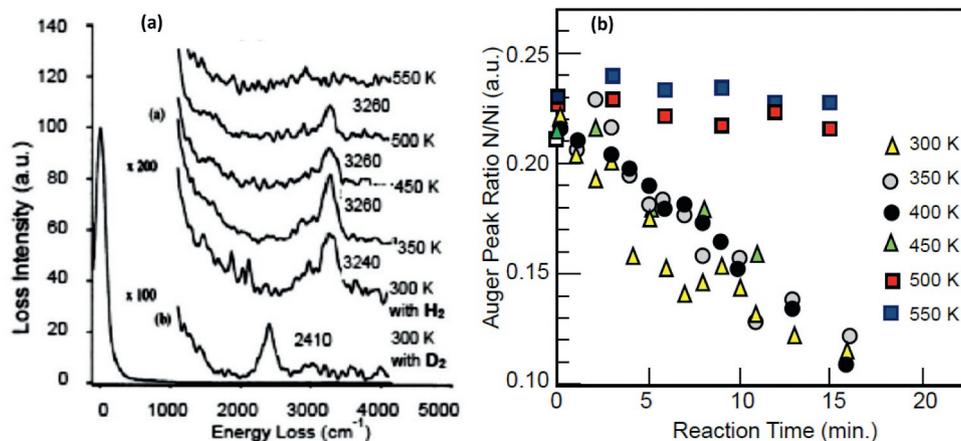


Fig. 4. (a) HREEL spectra of NH(a) observed below 550 K on a $p(2 \times 3)$ Ni(110)-N surface on exposure to H atoms; (b) N atom density on a $p(2 \times 3)$ Ni(110)-N surface decreases by a temperature-independent constant rate below 450 K on exposure to a flux of H atoms (attained in 2.0×10^{-6} Torr of H₂), but no decrease of N atoms occurs at temperatures above 500 K [33].

by $(\Delta G_i/\sigma_i)$, where “ σ_i ” is the “stoichiometric number” of each step. According to this mechanism, the decomposition reaction is given by the reverse process of Eq. (1), and the desorption of N₂ is the rate-determining reaction. The desorption rate of N₂ is described by the fugacity of N (P_{N^*}) on metals in the steady decomposition of NH₃, as described by Eq. (2).



$$\begin{aligned} K &= P_H^3 P_{N^*} / P_{NH_3}^2 \alpha P_{N^*} (1 - \theta_N)^2 = \theta_N^2 / \alpha P_{N^*} \\ &= \theta_N^2 / (1 - \theta_N)^2 \approx \theta_N^{2/\delta}; \theta_N \approx (\alpha P_{N^*})^{\delta/2} P_{N^*} \\ &= K P_{NH_3}^2 / P_H^3 \\ r &= k(\theta_N)^2 = k(\alpha P_{N^*})^\delta \\ &= k(\alpha K P_{NH_3}^2 / P_H^3)^\delta = k P_{NH_3}^x / P_H^y \quad (0 \leq \delta \leq 1.0) \end{aligned} \quad (2)$$

where P_H and P_{NH_3} are the pressures of H₂ and NH₃, N^* is Fe_xN and θ_N is the coverage in nitrogen atoms. The double arrows “ \rightleftharpoons ” indicate reversible reaction and the arrows in the both sides “ \rightleftharpoons ” indicate a barrier between the species in both directions. Here, α is the equilibrium constant of the dissociative adsorption of N₂ on metals, and K is the equilibrium constant of $2 NH_3 \rightleftharpoons N_2 + 3 H_2$. δ is an effective order, which varies in the range $0 \leq \delta \leq 1.0$ depending on the adsorption strength of N(a) on metals ($\delta = 1$ for weak adsorption and $\delta = 0$ for strong adsorption), and $(-\Delta H_0^\circ)$ is a general parameter relating to the heat of adsorption of various gases on metals [38].

The desorption rate of N₂ at coverage θ_N is given by $r = k P_{NH_3}^x / P_H^y$ in Eq. (2), where the exponent “ x ” varies from 0 to 1.5 depending on

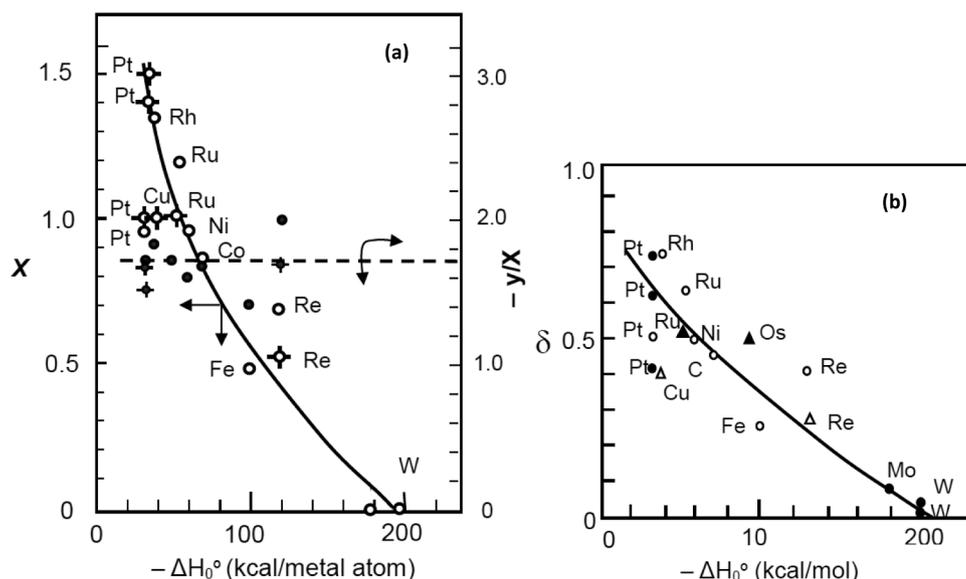


Fig. 5. (a) The (x) and (-x/y) values of the rate equation of $r = k P_{NH_3}^x P_H^y$ in the decomposition of NH₃ on various metals, which varies in relation to an empirical parameter representing the adsorption strength $(-\Delta H_0^\circ)$ [37]; (b) The δ -value in Eq. (2) varies from 1 to 0 depending on a parameter $(-\Delta H_0^\circ)$ related to the adsorption strength.

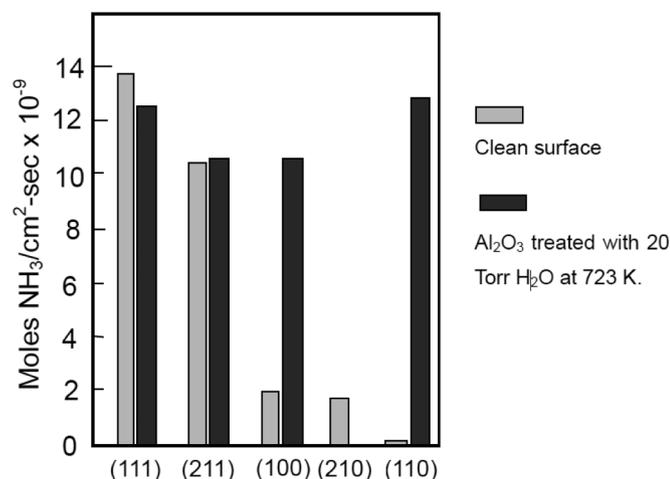
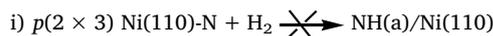


Fig. 6. The catalytic activity of Fe surfaces for the ammonia synthesis reaction depends markedly on the crystal plane. All crystal planes become as active as the Fe(111) plane after depositing 2 ML of Al₂O₃ followed by treating in H₂O vapor at 728 K [16,17].

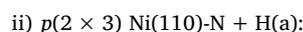
The activity of a catalyst is given by the number (density) of functional sites or materials acting catalytically. As discussed in detail below, the steady-state activity depends on the total number of labile quasi-compounds, [Fe_x] + [Fe_xN] + [Fe_xNH], on the surface. As shown in Fig. 5, the decomposition kinetics of NH₃ follows the rate-determining desorption of N₂ even if the metals have no activity for the synthesis reaction. As mentioned above, the precious metals and Ni are inactive for the synthesis of ammonia, but N(a) atoms and Ni₃N on these metals are hydrogenated to NH₃. Taking these results into account, we have to consider the required functions of a catalyst for the ammonia synthesis reaction.

The N₂ molecule does not dissociate on precious metals, nor on Ni. If precious metals and Ni are bombarded with N⁺ and/or N₂⁺ ions, N(a) atoms are adsorbed on precious metal surfaces without the formation of metal nitrides, but a quasi-compound of Ni₃N is formed on the Ni(110) surface. It should be pointed out that hydrogenation of adsorbed N(a) with H₂ on precious metals as well as the reaction of Ni₃N on Ni(110) with H atoms forms NH₃. Roman and Riwan [47] obtained a p(2 × 3) Ni(110)-N surface by bombarding a Ni(110) surface with N⁺ and/or N₂⁺ ions, and about a half-monolayer coverage of N(a) atoms was estimated. The p(2 × 3) Ni(110)-N surface prepared by bombarding N⁺ and/or N₂⁺ ions is not an array of adsorbed N(a) atoms, but an array of [Ni₃N] formed by the reaction of the Ni surface with N atoms. The rate of a reaction depends not only on the rate-determining slow step, but also on the coverage on the surface, and if labile quasi-

compounds are formed also on their quantity. For this reason, the hydrogenation of [Ni₃N] on Ni(110) is interesting. The hydrogenation of [Ni₃N] gives NH₃ via Ni₃NH, but Ni₃NH becomes unstable at temperatures higher than ca. 500 K. As a result, the Ni(110) surface covered with the quasi-compound Ni₃N becomes passive for reaction with H-atoms. This result shows that if N₂ molecules dissociate on Ni(110) at temperatures higher than 500 K, the surface is inactive for the ammonia synthesis reaction, because Ni₃NH cannot form above 500 K. Taking these results into account, we have to consider the role of labile quasi-compounds in the ammonia synthesis reaction, as discussed below:



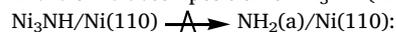
(No dissociation of H₂ on p(2 × 3) Ni(110)-N)



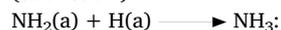
Hydrogenation equilibrium of quasi-compound in the temperature range of 300–500 K.



Irreversible decomposition of Ni₃NH (≥ 550 K)



A phase-change from quasi-compound Ni₃NH to adsorbed NH₂(a). (300–450 K)



Rapid hydrogenation of NH₂(a) on Ni(110) (300–450 K).



Adsorption equilibrium of NH₃.



Irreversible decomposition of quasi-compound Ni₃N at 830 K.

The p(2 × 3)Ni(110)-N surface fully covered with [Ni₃N] has no ability to dissociate H₂ molecules, which is similar to the low reactivity of [Cu₃N] on the Cu(110) surface with H₂ shown in Fig. 7 [46]. Adsorption of NO on the Cu(110) surface is similar to Ni(110). Cu₃N dots are randomly formed among a (2 × 1) array of (-CuO-) strings at room temperature, and the Cu₃N dots are ordered in a (2 × 3) array on the Cu(110) surface at 600 K, that is, the Cu(110) surface is covered with (-CuO-) strings in p(2 × 1) arrays and the Cu₃N dots form a p(2 × 3) array on the Cu(110) surface, as shown in Fig. 7(b). These quasi-compounds are rather stable at moderate temperatures, so that no catalytic decomposition of 2 NO → N₂ + O₂ takes place on the Cu(110) surface,

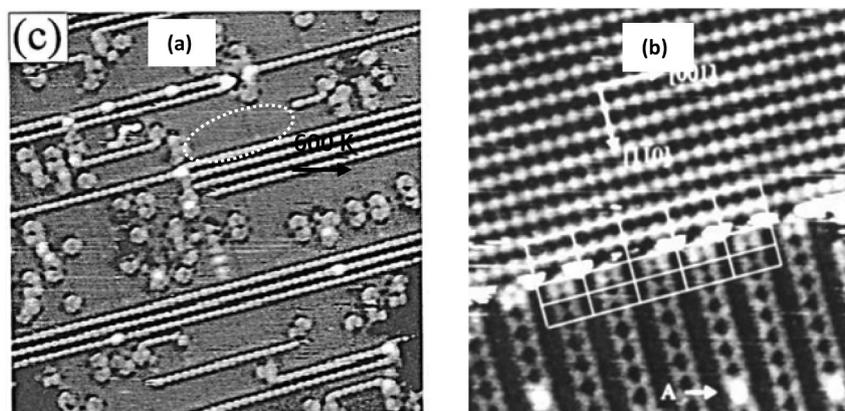


Fig. 7. (a) Adsorption of NO on a Cu(110) surface at room temperature. Cu₃N dots are randomly dispersed among a (2 × 1) array of (-CuO-) strings; (b) On raising temperature to 600 K, a hybrid array of (2 × 1)-(-CuO-) domains and p(2 × 3)Cu₃N clusters (rectangular mesh) are formed [46].

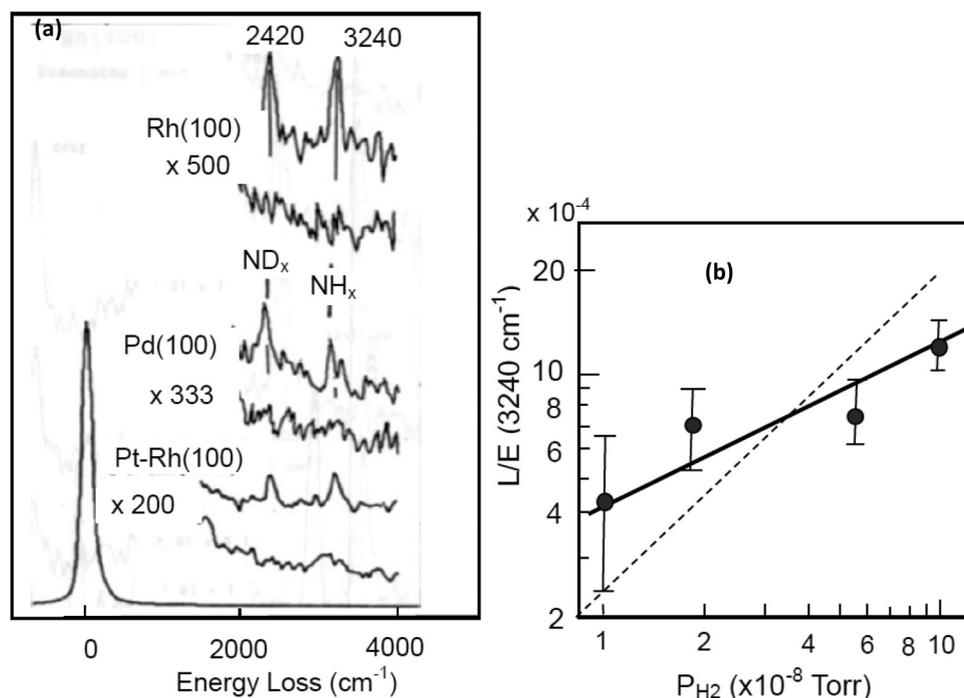


Fig. 8. (a) In situ HREEL spectra showing the formation of N–H and N–D observed by exposing $c(2 \times 2)$ Rh(100)-N, Pd(100) and Pt-Rh(100) surfaces to a 1:1 mixture of ($H_2 + D_2$) (10^{-7} Torr) at 400 K; (b) Intensity of electron energy loss peak as a function of H_2 pressure on Rh(100)-N surface; $P_{H_2}^{0.5}$ (solid line) and $P_{H_2}^{1.0}$ (broken line) [31,32].

although the overall reaction is thermodynamically favorable.

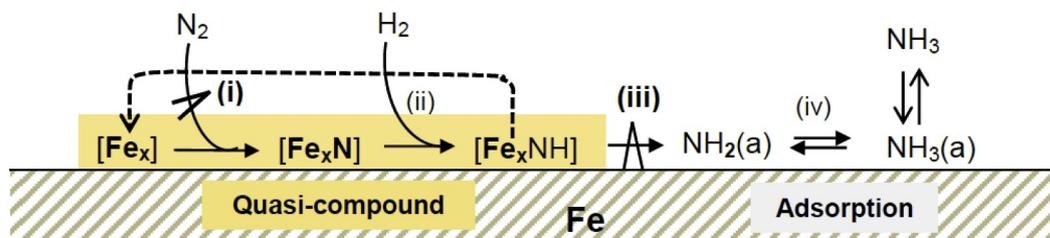
It is known that neither the dissociation of N_2 nor the formation of nitrides with N atoms occur on Pt(100), Pt(111), Pt(110), Pd(100) and Rh(100) surfaces, but the hydrogenation of adsorbed N(a) on these metals gives NH_3 , and the decomposition of NH_3 takes place on these precious metals. When a N(a)/Rh(100) surface was exposed to H_2 , formation of NH(a) was observed by high resolution electron energy loss spectroscopy (HREELS), and the intensity of the NH(a) peak changed according to the square root of hydrogen pressure $P_{H_2}^{1/2}$, as shown in Fig. 8(b). This indicates that the equilibrium $N(a) + 1/2 H_2 \rightleftharpoons NH(a)$ is established on the Rh(100) surface. Although the amount of N(a) was decreased by hydrogenation with H_2 , no $NH_2(a)$ was detected on the N(a)/Rh(100) surface. Similar phenomena were observed on the N(a)/Pd(100), N(a)/Pt(111), and N(a)/Pt-Rh(100) surfaces, that is, NH(a) was observed on these metals in the hydrogenation of N(a), but no detectable amount of $NH_2(a)$ was observed even though the amount of N(a) was decreased by forming NH_3 [31,32]. In contrast, $NH_2(a)$ was predominantly observed in the adsorption of NH_3 on these metals [48–50]. These results suggest the existence of a potential barrier in the reaction $NH(a) + H(a) \rightleftharpoons NH_2(a)$ on most metals, but the subsequent hydrogenation of $NH_2(a) + H(a) \rightarrow NH_3$ is very rapid, so that the amount of $NH_2(a)$ becomes lower than the detectable level during the hydrogenation of N(a). As shown in Fig. 5, the kinetics of the decomposition reaction of NH_3 given by $r = k(\alpha KP_{NH_3}^2/P_H^3)^{\delta}$ on these metals suggests that the desorption of N_2 is the rate-determining step.

Taking these results into account, we consider again the reaction of Ni_3N with H-atoms. As observed in Fig. 4, the amount of Ni_3NH decreased by hydrogenation to NH_3 , where the equilibrium $H + Ni_3N \rightleftharpoons Ni_3NH$ was established on the Ni surface during the decrease of Ni_3N , and the rate of decrease of Ni_3N was given by the flux of H-atoms. If the temperature was raised above 500 K, however, no more detectable NH(a) was observed on the Ni surface, and the decrease in the amount of Ni_3N was stopped. On the other hand, when the Ni(110) surface was exposed to NH_3 , two energy loss peaks assignable to $NH_2(a)$ were observed at 1520 cm^{-1} and 3240 cm^{-1} . These results strongly suggest the existence of a potential barrier between the quasi-compound ($Ni_3N + H \rightleftharpoons Ni_3NH$) and adsorbed $NH_2(a)$ on Ni. This would represent a kind of phase change, in the transformation of the quasi-compound Ni_3NH to

adsorbed $NH_2(a)$ on Ni, as summarized below.

Considering these results, we conclude that a high potential barrier exists in the conversion of the quasi-compound Ni_3NH to adsorbed $NH_2(a)$ on the Ni(110) surface, but the subsequent surface reaction of adsorbed $NH_2(a)$, $NH_2(a) + H(a) \rightleftharpoons NH_3$, is very rapid, not only on Ni but on most metals. These results strongly indicate that a catalyst active for the ammonia synthesis reaction should not only be active for the dissociation of N_2 , but all the other steps should be reversible at the given temperature.

The (2×2) Pd(100)-N, $c(2 \times 2)$ Rh(100)-N, and $c(2 \times 2)$ Pt-Rh(100)-N surfaces were also prepared by using the reaction of NO with H_2 , $NO + H_2 \rightarrow N(a) + H_2O$. The reaction was performed at a total pressure of 2–4 Torr at 500–600 K in a small-volume high-pressure reactor cell connected to the main UHV chamber. In the case of Pt no accumulation of N(a) atoms occurred, because the N(a) atoms deposited on Pt were very quickly consumed by hydrogenation to NH_3 . However, Amorelli et al. [51] accumulated N(a) atoms on a Pt(111) surface by the oxidation of NH_3 with adsorbed O(a), and Mudiyansele et al. [52,53] accumulated N-atoms on a Pt(111) surface by reaction of NH_3 with O_2 at 85 K, and a $p(2 \times 2)$ Pt(111)-N surface was attained by annealing at 400 K. A $p(2 \times 2)$ Pt(111)-N surface gave adsorbed NH(a) on exposure to H_2 , and N_2 was desorbed at 453 K. When the precious metals with adsorbed N(a) were exposed to a 1:1 mixture of $H_2 + D_2$ of 10^{-7} Torr at 400 K (lower than the migration temperature of N(a)), energy loss peaks assignable to NH(a) and ND(a) appeared at 3240 cm^{-1} and 2420 cm^{-1} ; however, the scissors modes for $NH_2(a)$ were below the detectable level, as shown in Fig. 8(a). A notable result was the intensity of NH(a) and ND(a) peaks, which were almost equal at a total pressure of 1×10^{-7} Torr ($H_2 + D_2$; $H_2/D_2 = 1$); that is, the apparent hydrogen isotope effect was very small [31,32]. The peak intensity of NH(a) on Rh(110)-N changed in proportion to $P_{H_2}^{1/2}$ as shown in Fig. 8(b), that is, an equilibrium of $N(a) + H(a) \rightleftharpoons NH(a)$ was established on the Rh(110)-N surface in the 10^{-8} Torr pressure range, but the apparent hydrogen isotope effect observed as NH(a)/ND(a) was very small when the hydrogen pressure was higher than 10^{-7} Torr, as shown in Fig. 8(a). How can these results observed on precious metals be rationalized? It should be pointed out that N(a) on precious metals exists in the form of adsorbed N(a) atoms rather than nitrides. One possible



Scheme 2. Dynamic model of the ammonia synthesis and decomposition reactions on Fe-catalyst: The rate determining step is the formation of labile $[\text{Fe}_x\text{N}]$, but the activity of the catalyst depends on the amounts of $[\text{Fe}_x\text{N}]$ and $[\text{Fe}_x\text{NH}]$ and their recycle rate, which is regulated by the potential barrier from a quasi-compound Fe_xNH to adsorption of $\text{NH}_2(\text{a})$ on Fe.

explanation is compensation of the isotope effect of $\text{NH}(\text{a})/\text{ND}(\text{a})$ by the isotope effect on the concentration of $\text{H}(\text{a})/\text{D}(\text{a})$ on metals.

In the scheme above it would seem that NH_3 would not affect the rate because its adsorption occurs after the rate-determining step. However, the adsorption of NH_3 forms adsorbed nitrogen atoms N^* and these compete for surface Fe_x sites involved in the formation of the surface compounds. Thus, NH_3 retards the rate as found experimentally.

If the ammonia synthesis on Fe catalysts is catalyzed by forming a labile Fe nitride (Fe_xN), the reaction of Fe_xN with H_2 should be different from the reaction of adsorbed $\text{N}(\text{a})$ with H_2 on precious metals. As discussed in this review, the ammonia synthesis reaction on Fe catalysts proceeds via the reaction of quasi-compounds ($\text{Fe}_x \rightarrow \text{Fe}_x\text{N} \rightleftharpoons \text{Fe}_x\text{NH}$), which is followed by formation of adsorbed $\text{NH}_2(\text{a})$ (Scheme 2). Therefore, the activity of the catalyst depends on the recycle rate of the quasi-compound $\text{Fe}_x\text{NH} \rightarrow \text{Fe}_x + \text{NH}_2(\text{a})$, but the kinetics is given by the rate-determining formation of Fe_xN , as described by the following reaction model.

A LEED pattern showed the formation of a $c(2 \times 2)\text{Cu}(100)\text{-N}$ surface by depositing N atoms on a Cu(100) surface, but STM results indicated an array of square Cu_3N patches ($5 \times 5 \text{ nm}$) separated by clean Cu(100) lines, like a checkerboard. Ni atoms deposited on this $c(2 \times 2)\text{Cu}(100)\text{-N}$ surface form nano-size Ni islands at the intersection of the clean Cu(100) lines without reacting with the square Cu_3N patches [54]. However, Fe atoms deposited on this $c(2 \times 2)\text{Cu}(100)\text{-N}$ surface react with Cu_3N to form iron nitride (Fe_xN) on the Cu(100) surface. As is known, Fe nitride (Fe_xN) takes on various stoichiometries and structures as a bulk compound: Fe_3N (hcp), Fe_2N (orthorhombic), Fe_4N (fcc), and FeN (ZnS and rocksalt structures), and the epitaxial growth of Fe_xN [55–57], FeN [58,59], and Fe_2N [60] has been reported. The catalytic ability of Fe_xN on Cu(110) may depend on “x”, but it is difficult to identify the Fe_xN stoichiometry working as the catalyst, because the Fe atoms released by the hydrogenation of Fe_xN are quickly dissolved into the Cu(100) crystals.

How can the inverse hydrogen isotope effect of $r_{\text{D}}/r_{\text{H}} = 2\text{--}3$ observed by Ozaki, Taylor and Boudart [36] on a doubly-promoted $\text{K}_2\text{O}/\text{Al}_2\text{O}_3/\text{Fe}$ catalyst at 486–575 K be rationalized? According to the Langmuir-Hinshelwood description, the inverse hydrogen isotope effect in the dissociation of N_2 is given by $r = P_{\text{N}_2}(1 - \theta_{\text{NH}})^2$, where the ratio of $\theta_{\text{NH}}/\theta_{\text{ND}} > 1$. However, the apparent intensity of $\text{NH}(\text{a})$ and $\text{ND}(\text{a})$ peaks on the N/Rh(100), N/Pd(100), and N/Pt-Rh(100) surfaces in a 1/1 mixture of ($\text{H}_2 + \text{D}_2$) showed no apparent isotope effect, as shown in Fig. 8(a). This result suggests that $[\text{Fe}_x\text{N}] + \text{H}(\text{a}) \rightleftharpoons [\text{Fe}_x\text{NH}]$ and $[\text{Fe}_x\text{N}] + \text{D}(\text{a}) \rightleftharpoons [\text{Fe}_x\text{ND}]$ may show a rather large hydrogen isotope effect, but the isotope effect for adsorbed $\text{NH}(\text{a})$ and $\text{ND}(\text{a})$ on metals is compensated by that of $\text{H}(\text{a})/\text{D}(\text{a})$ on the metals. If this is the case, the ratio of $[\text{Fe}_x]_{\text{H}}/[\text{Fe}_x]_{\text{D}} < 1$ in the steady-state reaction. Thereby, the Eq. (1) can be further described as Eq. (3). Nevertheless, it should be recognized that surface science result may not provide the direct evidence for this proposal, but this result may provoke further research, such as *in-situ* spectroscopic measurements.



4. Conclusions

For the NH_3 decomposition reaction, the kinetics of the decomposition involves the rate-determining desorption of N_2 , in either the decomposition of quasi-compounds or the desorption of adsorbed $\text{N}(\text{a})$, that is, $\text{Fe}_x\text{N} \rightarrow \text{Fe}_x + 1/2 \text{N}_2$ on Fe and $2 \text{N}(\text{a}) \rightarrow \text{N}_2$, on precious metals, and the kinetics is given by a common equation expressed by $r = k(\theta_{\text{N}})^2 = k(\alpha P_{\text{N}^*})^2 = k P_{\text{NH}_3}^x / P_{\text{H}}^y$ in Eq. (2), but the ammonia synthesis reaction is quite different. That is, the formation of labile metal nitrides such as Fe_xN and Fe_xNH is indispensable, so that if a labile compound is decomposed at elevated temperature, no NH_3 formation takes place even if the quasi-compound Ni_3N exists. Furthermore, a combination of spectroscopic studies may be necessary to clarify whether the quasi-compounds can be formed under real ammonia synthesis/decomposition conditions.

Conflicts of interest

There are no conflicts to declare.

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Supplementary materials

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