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LR SPECTROSCOPIC STUDY OF CHEMISORBED DINITROGEN SPECIES ON AMMONIA SYNTHESIS IRON CATALYSTS *

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The results of the LRS study of N-containing chemisorbed species on the promoted iron catalyst for ammonia synthesis have further substantiated the existence of two species of $N_2(a)$ as the dominant N-containing chemisorbed species under the functioning catalyst conditions. A model of active site, as 3-Fe cluster on (111) or (211) surface of α-Fe, and two modes of multinuclear coordination activation for the observed two species of $N_2(a)$ were proposed. It was further illustrated from reaction energetics that the mechanism of the dominant reaction pathway for ammonia synthesis/decomposition may be associative, rather than dissociative.

Ammonia synthesis iron catalysts, Raman spectroscopy

1. Introduction

Chemisorbed species of dinitrogen, $N_2(a)$, are among key intermediates in ammonia synthesis over iron catalysts. Knowledge about their nature and relative abundances on the functioning surface of iron catalysts has significant implications concerning the nature of the active site of the catalyst and the general understanding of the reaction mechanism of ammonia synthesis/decomposition.

The existence of chemisorbed species of $N_2(a)$ and its partially hydrogenated derivatives, $N_2H(a)$, etc., has been inferred by many investigators. Schmidt[1] showed that the FM spectra of an iron tip, treated at 200 ° C with NH_3, indicated the presence of $N_2H_x^+$ as some of the major species; Brill et al. [2] observed the IR spectra of chemisorbed species which were assigned to a hydrazine-like surface species; Morikawa and Ozaki[3] observed that chemisorbed $^{30}N_2(a)$ on iron

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catalysts could be displaced with gaseous $^{28}N_2$ at 380 ° C; and more recently, the presence of adsorbed molecularly N_2(a) on iron catalysts was inferred by Toyoshima[4] from his thermal-desorption rate experiment and the exchange reaction rate between $^{28}N_2$ and $^{30}N_2$ on promoted and unpromoted iron catalysts at 350–450 ° C in the presence of H_2.

Chemisorption of N_2 on single-crystal and polycrystalline iron surface at low temperature has been extensively studied by means of photoemission spectroscopy [5,6], XPS and UPS [7]. The results indicated the existence of a molecularly chemisorbed N_2(a) species as a precursor of atomically chemisorbed N(a) species, and gave a reasonable mechanistic interpretation of the dissociative chemisorption of N_2(a) on α-Fe at low pressure in the absence of H_2. More recently, Whitman et al. [8] studied the adsorption of N_2 on K-precovered Fe(111) at 74 K with HREELS and TDS and found that low coverages of K caused an increase in the maximum population of α-N_2(a).

According to Ertl [9], chemisorbed NH(a) began to decompose into N(a) and H_2 at 120 ° C, and the surface concentration of N(a) on α-Fe(111) exposed to the flowing stream of $N_2/3H_2$ at 310 ° C and near atmospheric pressure appeared to be very small.

Thus, the assumption of either N(a) or NH(a) as the major chemisorbed species on ammonia synthesis iron catalysts remains to be justified, as has been pointed out by us [10], and the explanation of the known reverse deuterium isotope effect of the ammonia synthesis reaction, first observed by Ozaki, Taylor and Boudart [11] and later confirmed by many other investigators, on the dissociative reaction mechanism and thermodynamic ground is open to question [10]. Formal kinetic study is not a good criterion for discriminating between the two possible mechanistic interpretations, dissociative and associative, because kinetic equations derived from them may be quite similar. For the resolution of the mechanistic controversies, in-situ measurements of the relative abundances of N(a), NH(a), and N_2(a) under ammonia synthesis reaction conditions are needed.

Recently, the in-situ LRS studies in our lab [12] and in Schrader's lab [13] provided new information about the nature of the surface species involved in iron-hydrogen, iron-nitrogen, and nitrogen-nitrogen bondings; the results showed that, under the reaction condition of 400–450 ° C and atmospheric pressure for ammonia synthesis/decomposition, the observable chemisorbed species in either case appear to be two species of H(a) and two species of N_2(a) rather than N(a) or NH(a). In the present work, behavior of these N_2(a) species on the functioning surface of an industrial double-promoted iron catalyst for ammonia synthesis, A_{110-3}, is further investigated in-situ by means of LRS at 400–450 ° C and atmospheric pressure in stationary gaseous systems of $1N_2/3H_2$ and $10N_2/1H_2$ and flowing gaseous system of $1N_2/3H_2$ at various space velocities. The results are discussed together with the nature of active site of the iron catalyst and the model(s) of coordination-activation of N_2(a), as well as reaction energetics and the dominant reaction pathway of ammonia synthesis/decomposition.

2. Experimental

The sample of a typical double-promoted fused-iron catalyst, A_{110-3}, for industrial ammonia synthesis was used in this investigation. Prior to obtaining the Raman spectra, samples underwent a reduction pretreatment in a controlled-atmosphere quartz cell, such as described previously [12,13], using a flow of purified H_2 at atmospheric pressure at 120 ° C for 2 h, 250 ° C for 2 h, 350 ° C for 8 h, and finally 450 ° C for a minimum of 24 h. The surface area of the reduced catalyst was 15 m^2/g.

Raman spectra of chemisorbed species on the catalyst were taken by exposing the samples to flowing or static H_2, N_2, $1N_2/3H_2$, or $10N_2/1H_2$. The N_2 and H_2 used in this study was research grade. The gases were further purified by passing them through a Deoxo purifier and a molecular sieve trap.

A Spex Ramalog-6 laser Raman spectrometer was used. The 514.5 nm line from a Spectra Physics Model 164 argon ion laser was used as the excitation source with an intensity of about 300 mW measured at the source. Slit width settings correspond to a resolution of 4 cm^{-1}. The spectrometer was interfaced with a Datamate system for recording spectra. The setting of samples made the angle of collection of Raman radiation 90 °. The reduction of the catalyst samples and chemisorption experiments, as well as Raman spectra measurements, were conducted in-situ. The details about the experimental procedure had been described in the previous paper [12].

3. Results and discussion

3.1. RAMAN SPECTRA OF N-CONTAINING CHEMISORBED SPECIES

In fig. 1a is shown the Raman spectrum of adspecies in the region of 1850–2350 cm^{-1} on the functioning iron catalyst after 8 h of ammonia synthesis at 450 ° C and then cooling to room temperature, in which conspicuous Raman peaks were observed at 1902, 1940, 1951, 2035, 2160, and 2331 cm^{-1}. This spectrum was consistent with the results reported previously by Liao et al. [12] and by Zhang and Schrader [13]. The peak at 2331 cm^{-1} was due to free gaseous N_2 existing in the atmosphere associated with the sample compartment region of the spectrometer; this peak may conveniently be used as a reference. The peaks at 1902 and 1951 cm^{-1} may be ascribed to Fe–H stretches due to two H(a) species, and the peaks at 1940 and 2035 cm^{-1} were assignable to N≡N stretches due to two N_2(a) species, as have been proposed previously [12,13].

In order to make the concentration of N_2(a) species on the surface as high as possible in favor of spectroscopic measurement, a sample of A_{110-3}, which had worked under reaction conditions of ammonia synthesis for 8 h, was exposed to a flow of $10N_2/1H_2$ gaseous mixture for 15 min, and subsequently cooled down to

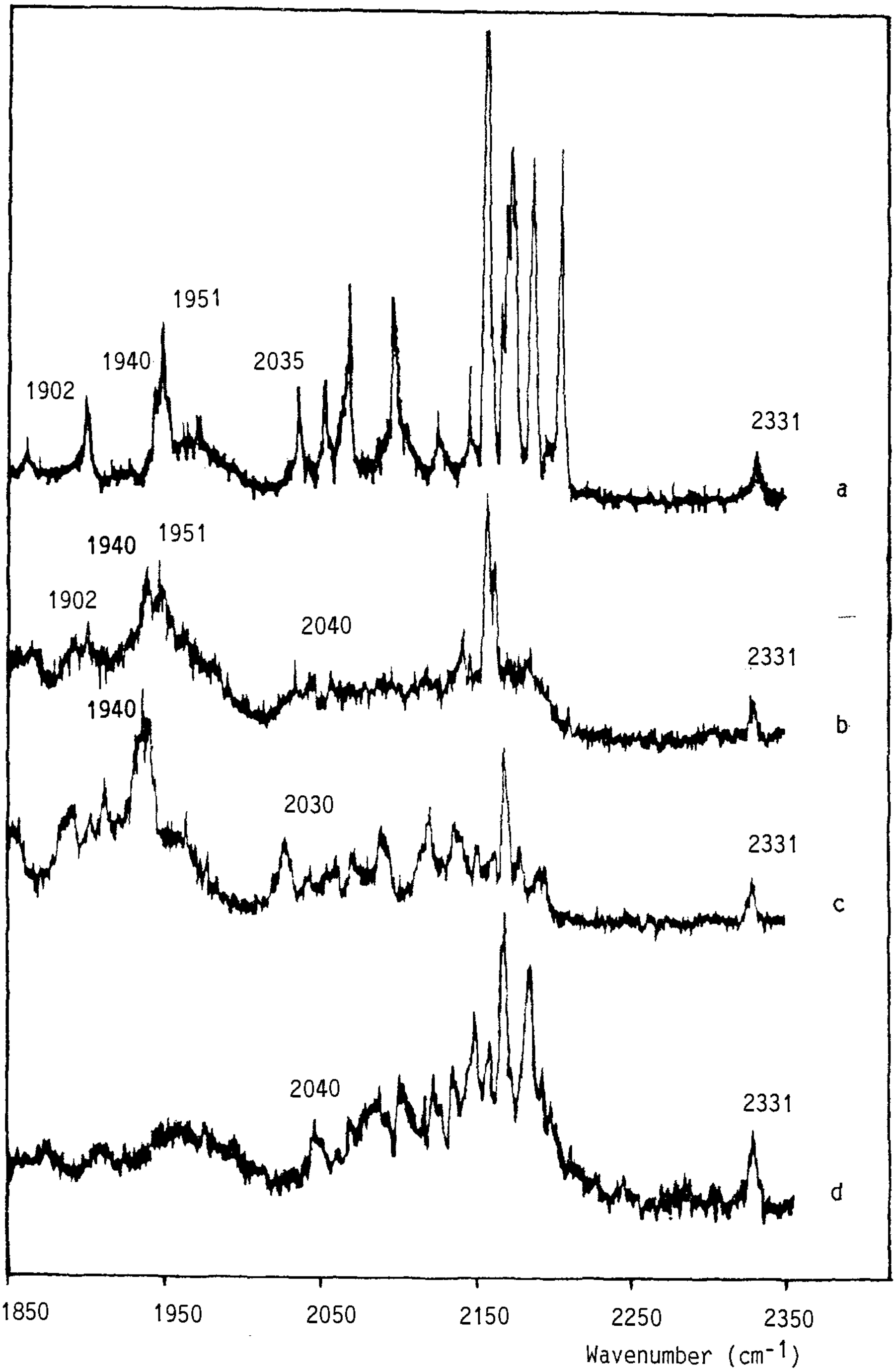


Fig. 1. Raman spectra (obtained at room temperature) of adspecies on the promoted iron catalyst A_{110-3}:

a) after ammonia synthesis at 450 °C in a flow of $1N_2/3H_2$ for 8 h;
b) followed after 1a) by exposure to a flow of $10N_2/1H_2$ at 450 °C for 15 min;
c) heating after 1b) to 450 °C statically in the remaining atmosphere of $10N_2/1H_2$ for additional 20 min;
d) followed after 1c) by exposure to a flow of purified N_2 at 450 °C for 20 min.

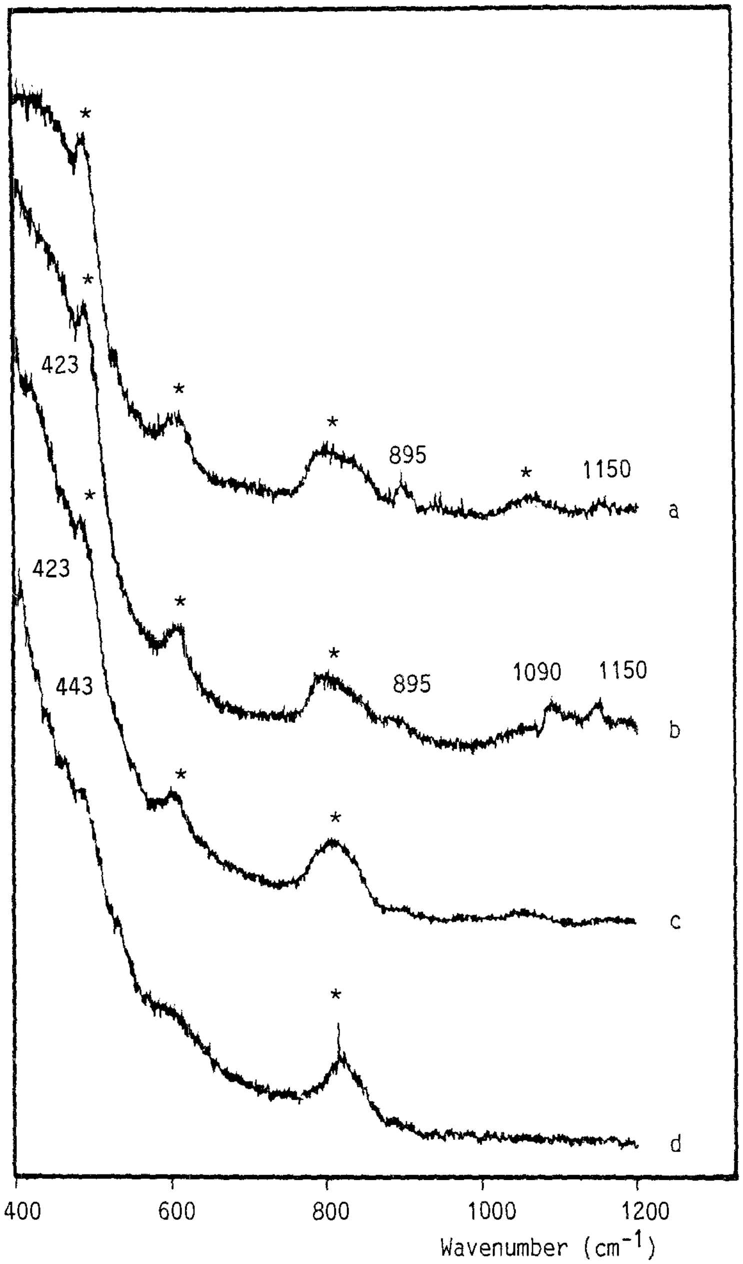


Fig. 2. Raman spectra of adspecies on the promoted iron catalyst A_{110-3}:

a) taken under the same conditions as 1b);

b) taken under the same conditions as 1d);

c) functioning for ammonia synthesis at 450 ° C and atmospheric pressure in $1N_2/3H_2$ feed gaseous mixture;

d) followed after 2c) by cooling to room temperature.

(Raman peaks marked with star (*) at 1060, 800, 602, and 491 cm^{-1} were due to the quartz cell; no Raman peak due to the catalyst in the regions of 400–1200 and 1850–2350 cm^{-1} was observed).

room temperature as rapidly as possible for acquisition of spectrum. The resulting spectra were shown in fig. 1b and 2a, in which the intensity of the peak at 1940 cm^{-1} was obviously enhanced and, meanwhile, two new peaks appeared at 1150 and 895 cm^{-1}. On continuing to heat this sample statically in the remaining atmosphere of $10N_2/1H_2$ to 450 °C for additional 20 min, the Fe–H peaks at 1951 and 1902 cm^{-1} were dramatically weakened, finally disappeared; on the other hand, the N≡N stretch peaks at 2030 cm^{-1}, especially at 1940 cm^{-1}, became stronger, as shown in Figure 1c. This reflected the depletion of H(a) on the surface of the catalyst and was consistent with the composition of the feed gaseous mixture with a high ratio of N_2 to H_2 (10 : 1 v/v). Interestingly, the 1940 cm^{-1} peak vanished after this sample was exposed to a flow of purified N_2 at 450 °C for 20 min (fig. 1d); meanwhile, the peak at 895 cm^{-1} was also weakened but the intensity of 1090–1150 cm^{-1} region was somewhat enhanced (fig. 2b), indicating nitridation of the surface.

Note that the Raman peaks at 895 cm^{-1} and 1090–1150 cm^{-1} region have been assigned by Zhang and Schrader [13], according to the recent LRS study of NH_3/Fe systems, to Fe–N stretches of two species, NH(a) and N(a), respectively. However, the two peaks were absent both in the spectrum taken in-situ on this catalyst working under the reaction conditions for ammonia synthesis at 400–450 °C and atmospheric pressure in flow of $1N_2/3H_2$ gaseous mixture (fig. 2c) and in that taken after cooling to room temperature (fig. 2d). This result is noteworthy: it indicates that N(a) and NH(a) were present in detectable surface concentrations only when the catalyst was exposed to N_2 containing a small amount of H_2; while, neither N(a) nor NH(a) was detectable on the functioning surface of the catalyst under reaction conditions of ammonia synthesis at 400–450 °C and atmospheric pressure.

A satisfactory assignment for the peaks in 2060–2250 cm^{-1} region observed statically at room temperature can not be made at present (although N≡N stretch peak of weakly adsorbed N_2(a) at some sites of the inhomogeneous surtace were expectable to occur in this region); these peaks did not occur in the dynamical spectra taken in-situ at high temperature under the functioning catalyst conditions.

It is also interesting to note the dependence of the peak intensity on the space velocity of $1N_2/3H_2$ feed gaseous mixture. It is conceivable that enhancing the s.v. of the feed gaseous mixture could be expected to make the ammonia synthesis reaction system further removed away from the equilibrium state, resulting in enhancement of steady concentration of intermediate species before the r.d.s. on the catalyst surface, and, at the same time, in decreasing that of intermediate species behind the r.d.s.. Such behavior was shown in fig. 3, where the 1940 cm^{-1} peak appeared only as a shoulder near to the strong Fe–H peak at 1951 cm^{-1} when the GHSV of the feed gaseous mixture was 12000 ml $1N_2/3H_2$ at 25 °C and atmospheric pressure/ml catalyst-h (fig. 3a), and became a distinct peak when the GHSV used was 18000 ml $1N_2/3H_2$ at 25 °C and atmospheric

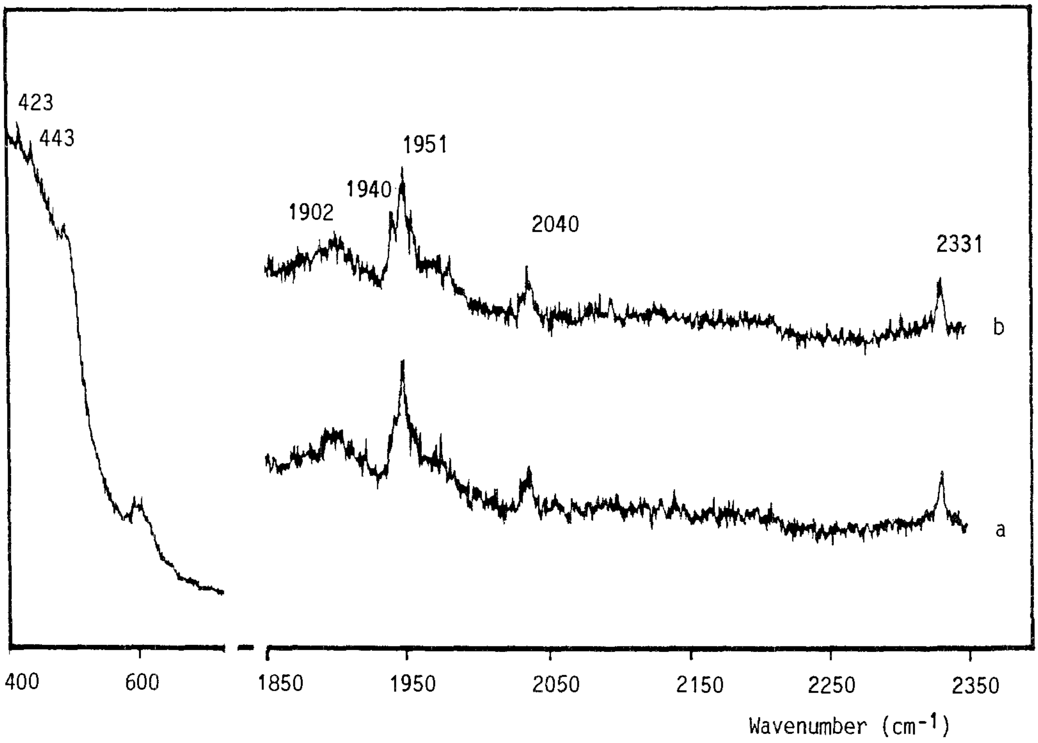


Fig. 3. Raman spectra of species adsorbed on the promoted iron catalyst A_{110-3} taken in-situ at 450 °C and atmospheric pressure; variation in $1N_2/3H_2$ flow rates (ml $1N_2/3H_2$ 25 °C, 1 atm/ml catalyst-h): a) 1200; b) 18000.

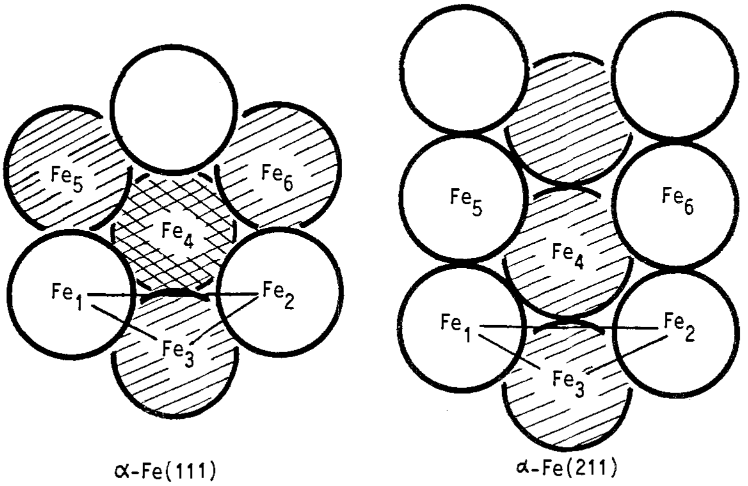
pressure/ml catalyst-h (fig. 3b). Such dynamical spectral behavior indicated that the N_2(a) species concerned with 1940 cm^{-1} peak was probably intermediate species before the r.d.s.

The experimental results described above and in the previous papers [12–14] show that, under the reaction conditions of ammonia synthesis, the surface concentrations of N(a) and NH(a) are both below the detectable limit of the Raman spectroscopy, which can be observed only when the catalyst was exposed to pure N_2 (in the presence of trace of chemisorbed H(a)), or to $10N_2/1H_2$ in our experiments, and that the molecularly chemisorbed N_2(a) species, with the corresponding $\nu_{N\equiv N}$ (Raman) at 2040 and 1940 cm^{-1} and ν_{Fe-N} at 423 and 443 cm^{-1}, respectively (see fig. 3), appear to be the most abundant N-containing adspecies on the surface of the functioning catalyst, in our opinion, also the dominant *reactive* N-containing species on the surface before the r.d.s. of the ammonia synthesis reaction.

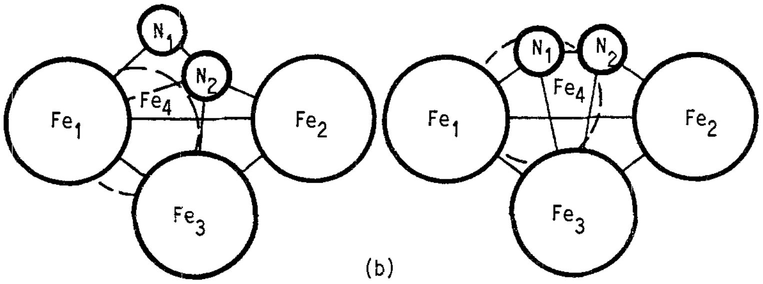
3.2. NATURE OF ACTIVE SITE AND DOMINANT REACTION PATHWAY

The observed large reduction in N≡N stretch frequency from 2331 cm^{-1} for free N_2 to 2040 or 1940 cm^{-1} for N_2(a) seems to indicate multinuclear coordination-activation of the N≡N triple bond. Thus, it may be inferred that the active site must be ensemble consisting of several iron atoms, probably with proper cluster structural form, and must be able to provide certain mode(s) for effective activation of N_2 molecule through multinuclear coordination. One may argue that the active sites might be surface defects, or steps and kinks sites, so small in number that the reactive adspecies on these sites might not be detectable by means of IR or Raman spectroscopy. However, this argument seems to be untenable in view fo the very pronounced structure sensitivity of ammonia synthesis reaction over iron catalyst, as evidenced by the experimental fact that the α-Fe(111) surface plane exhibits the highest activity [15] and the highest rate of N_2 chemisorption [5], that the catalytic activity actually decreases, rather than increases, with increasing dispersion [16], and that, even in the presence of promoter atoms (K), there is still a marked anisotropy in the ammonia synthesis activity of iron single-crystal planes [17,18]. The recent in-situ X-ray diffractometry investigation, carried out by Rayment et al. [19], showed that, even though in the case of the real (promoted) iron catalyst, in addition to a new, rather broad, peak at $2\theta \sim 25°$, which appeared irrespective of whether the reduction of the catalyst was carried out, the characteristic X-ray diffraction peak at $2\theta \sim 45°$ for α-Fe(110) spacing (0.5 × 4.05 Å) remains observable and identifiable, although this peak was considerably broadened, probably due to paracrystallinity of the catalyst under reaction conditions and the presence of dissolved hydrogen or internally adsorbed hydrogen ($\underline{H}$). This indicated that the promoted catalyst possesses essentially no long-range atomic order, but microcrystalline particles of α-Fe (about 20 Å diameter) may still exist, with the requisite Fe_x-cluster ensemble for effective coordination-activation of N_2.

In view of the results reported recently by Somorjai et al. [20] that the α-Fe(211) surface is almost as active as the α-Fe(111) surface, to first approximation, an active site may be regarded as a 3-Fe cluster as that on (111) or (211) surface (shown in fig. 4a), with each of the 3-Fe within bonding distance to the N_2(a). From known data of N≡N bond length and vibrational frequencies in some N_2-complexes, the N–N bond length of the observed two major N_2(a) species may be estimated from 1.098 Å for free N_2 to be extended to 1.15 Å. The Raman peak wavenumber 2040 cm^{-1} is close to the IR peak wavenumber 2050 cm^{-1} for $\nu_{N\equiv N}$ of N_2(a) on Fe/MgO observed by Tamaru et al. [21], thus this 2040 cm^{-1} Raman peak has probably arisen from a N_2(a) species chemisorbed on the catalyst A_{110-3} in a mode similar to that of the N_2(a) species on Fe/MgO. Since this vibrational mode ($\nu_{N\equiv N} = 2040$ cm^{-1}) appears to be both Raman and IR active, it is attributable to an unsymmetrical single-end-on, or single-end-on-plus-side-on, coordination mode on α-Fe surfaces, including some of the Fe atoms constituting the ammonia-synthesis active sites. In contrast with the case of 2040 cm^{-1} peak, no distinct and identifiable IR band for N_2(a) around 1940 cm^{-1} has been reported so far, thus this Raman-active vibrational mode is probably IR inactive, pending further in-situ FT–IR confirmation. Thus, this



(a) $r(Fe_1-Fe_2)=4.05$Å; $r(Fe_1-Fe_4)=r(Fe_2-Fe_4)=2.87$Å;
$r(Fe_1-Fe_3)=r(Fe_2-Fe_3)=r(Fe_3-Fe_4)=2.48$Å.



Mode I $\mu_3(\eta^2,\omega)$-$N_2(a)$ (γ')
$r(N_1-N_2)=1.15$Å;
$r(N_1-Fe_1)=2.0$Å;
$r(N_2-Fe_2)=r(N_2-Fe_3)=1.9$Å.

Mode II $\mu_3(\eta^2,\omega,\omega')$-$N_2(a)$ (α')
$r(N_1-N_2)=1.15$Å;
$r(N_1-Fe_1)=r(N_2-Fe_2)=1.8$Å
$r(N_1-Fe_3)=r(N_2-Fe_3)=1.9$Å.

Fig. 4. The vertical view of the proposed 3-Fe cluster active site on α-Fe (111) or (211) surface and the two multinuclear coordination modes proposed for the observed chemisorbed N_2-species: $\mu_3(\eta^3, \omega)$-N_2 and $\mu_3(\eta^2, \omega, \omega')$-$N_2$.

may be ascribed to a flat-lying double-end-on, or double-end-on-plus-side-on, supported-bridge type coordination mode, as inferred previously by us [10,12,14]. These two modes (symbolically expressed as γ' and α') suggested above for the two observed species of $N_2(a)$ are shown diagrammatically in fig. 4. It is interesting to note that the flat-lying mode (Mode II) is quite similar to that of the μ_3-$N_2(\eta^2)$ in the Ti_4-complexes reported by Pez et al. [22], and emphasizes a more open cluster-structural active-site with Fe(1) and Fe(2) at a distance of 4.05 Å as a key structural parameter for double-end-on coordination of α'-$\underline{N}_2$ to the active site of ammonia synthesis iron catalysts. This is also in accord with the known surface-structural sensitivity. The favorable coordination activation of such a model is also supported by an approximate quantum-chemical calculation [23].

The results described above, together with the known inverse deuterium isotope effect [11] and stoichiometric number [24], favor an associative mechanism for the dominant reaction pathway of ammonia synthesis over the iron catalyst, with partial hydrogenation of $N_2(a)$ as r.d.s., which can easily interprete the inverse deuterium isotope effect on kinetic ground without resort to the arbitrary assumption of NH(a) and/or N(a) being the most abundant reaction intermediate. The low surface concentration of N(a) with $1N_2/3H_2/\alpha$-Fe does indicate that the formation of N(a) by dissociative chemisorption is slower than the hydrogenation of N(a), but this does not exclude the possible existence of a parallel reaction pathway, an associative reaction pathway with hydrogen-assisted dinitrogen dissociation, as the dominant pathway.

As pointed out previously, under the actual reaction conditions of ammonia synthesis, the situation of the real surface of the catalyst is quite different from that of surface under high vacuum conditions, because of the "pressure gap" [25] and the presence of large amount of H(a) [26], as evidenced by the fact that industrial ammonia synthesis iron catalysts can operate for years without much deactivation, whereas iron catalysts, when exposed to $1N_2/3H_2$ at low pressure ($\leqslant 10^{-6}$ Torr), rapidly deactivate due to formation of surface nitride [25]. On a functioning catalyst surface in the presence of considerable amounts of H(a) and other chemisorbed species, reorientation of γ-$\underline{N}_2(a)$ to α'-$\underline{N}_2(a)$ or γ''-$\underline{N}_2(a)$ may require higher activation energy than in the case of $\underline{N}_2(a)$ on bare surface; while on the other hand, it would facilitate partial hydrogenation of the $N_2(a)$ by transfer of H(a) to the exo-N probably with accompanying formation of additional Fe-N bonding, so as to partially stabilize the highly unstable reaction intermediate, $\underline{N}_2H(a)$, and to lower the activation energy barrier of the key initial-step of partial hydrogenation. Consequently, before undergoing dissociation, these $N_2(a)$, flat-lying, especially the inclinedly mounting, species may have plenty of chances to react with certain H(a), probably $H^{\delta+}(a)$, to form $\underline{N}_2H(a)$ or $\underline{N}_2H_2(a)$ as a r.d.s., followed by rapid hydrogen-assisted-dissociation to $\underline{N}(a) + \underline{N}H_2(a)$, or $\underline{N}H(a) + \underline{N}H(a)$, or $\underline{N}H(a) + \underline{N}H_2(a)$, or $\underline{N}H(a) + \underline{N}H_3(a)$, finally, to $2NH_3$. Note that, with cluster-structural model, $\underline{N}_2H(a)$ and $\underline{N}_2H_2(a)$ are not restricted to coordinate single-end-on. A double-end-on mode would remove the objection that the formation of these highly unstable intermediates, $\underline{N}_2H(a)$ and $\underline{N}_2H_2(a)$, is energetically unfavorable. Based upon relevant bonding energies listed in table 1, a potential energy diagram for ammonia synthesis on iron catalysts corresponding to the dominant reaction pathway is constructed in fig. 5.

In the case of ammonia decomposition, as proposed by Zhang and Schrader [13], reaction pathway going through combination of two non-mobilized N(a), which is situated at a "dead-valley" of the potential energy diagram (Figure 5) and known to be stable to pumping at a temperature as high as 310°C [9], to form $\underline{N}_2(a)$ is apt to be considerably less favorable energetically than an alterna-

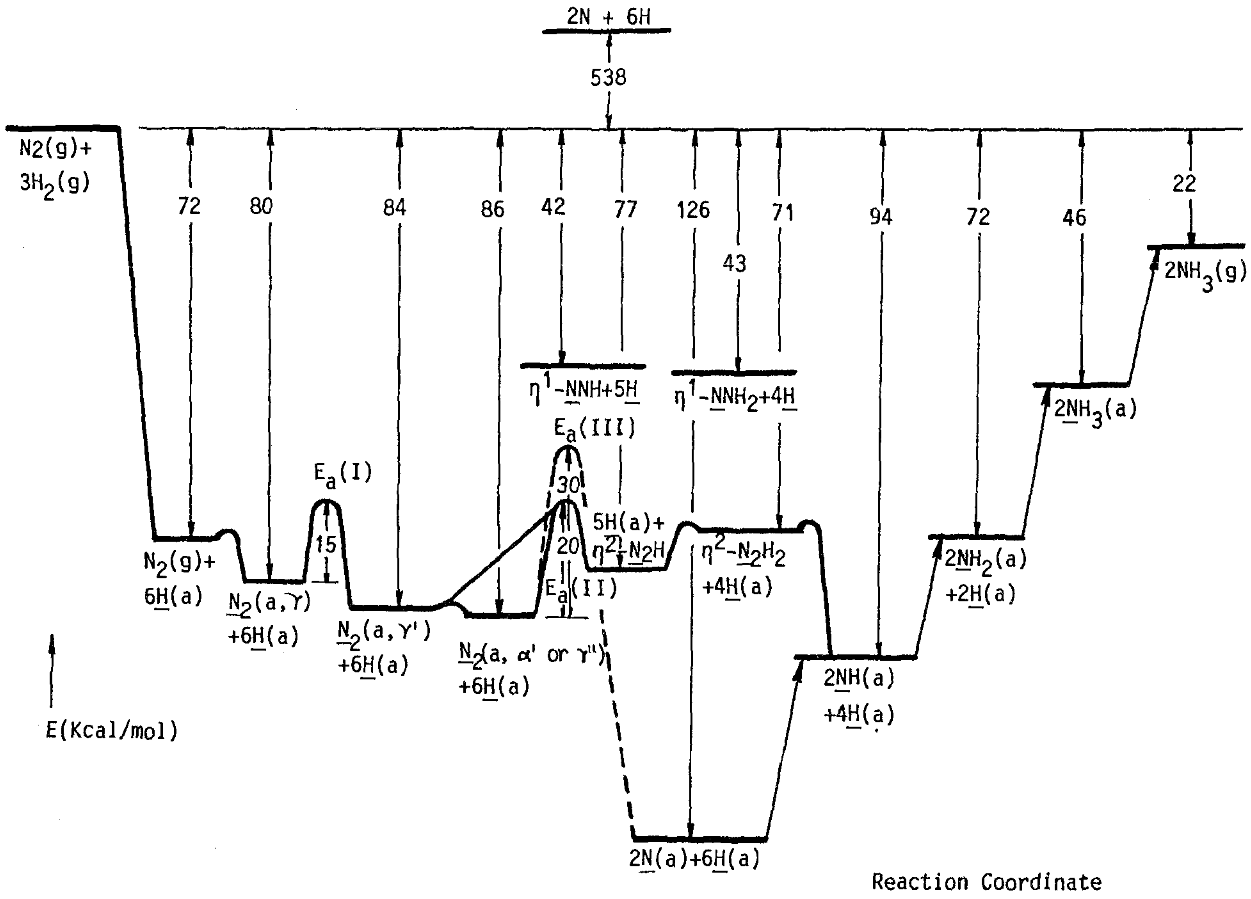
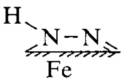
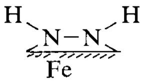
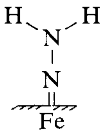


Fig. 5. A potential energy diagram for ammonia synthesis on iron catalysts with the associative mechanism as the dominant reaction pathway.

Table 1
Bonding energies (in kcal/mol) for estimation of the potential energy diagram for ammonia synthesis on iron catalyst

N≡N	226	Fe–[$\underline{H}$(a)]	64	$Q_{ad}[\underline{N}_2$(a, γ)]	8 **	$Q_{ad}[\underline{N}_2H_2$(a)]	16 ***
N=N	100	Fe–N[$\underline{N}$(a)]	140 *	$Q_{ad}[\underline{N}_2$(a, γ')]	~12 ***	E_a(I)	15 **
N–N	27	Fe–N[$\underline{N}$H(a)]	100 *	$Q_{ad}[\underline{N}_2$(a, α' or γ'')	14 ***	E_a(II)	20 **
H–H	104	Fe–N[$\underline{N}H_2$(a)]	65 *	$Q_{ad}[\underline{N}$(a)]	140 ***	E_a(III)	30 ***
N–H	93	Fe–N[$\underline{N}H_3$(a)]	12 *	$Q_{ad}[\underline{N}$H(a)]	100 *	E_d(III)	70 ***

$\underline{N}_2$(a, γ') Total B.E. = 238 *** $\nu_{N-N} = 2040\ cm^{-1}$		$\underline{N}_2$(a, α' or γ'') Total B.E. = 240 *** $\nu_{N-N} = 1940\ cm^{-1}$		$\underline{N}$NH(η^1) Total B.E. = 260*	
$\underline{NN}$H(η^2) Total B.E. = 295		H$\underline{NN}$H(η^2) Total B.E. = 353		$\underline{N}$NH(η^1) Total B.E. = 325	

* Ref. [5]; ** ref. [28]; *** Estimated by means of the BOC Model [29,30], e.g., $Q^0_N = 80$ [$= Q_N/(2-\frac{1}{n})$, n = 4) for $\underline{N}$(a), etc...

tive reaction pathway going through combination of $\underline{N}$H(a) with $\underline{N}H_3$(a) to form H$\underline{NN}H_3$(a) or of two less firmly localized $\underline{N}$H(a) to form H$\underline{NN}$H(a), followed by rapid dehydronation of these species and desorption of $\underline{N}_2$(a) and $\underline{H}_2$(a), or 2$\underline{H}_2$(a). The $\underline{N}$H(a) + $\underline{N}H_3$(a) pathway is analogous to the reaction pathway of ammonia decomposition on polycrystalline tungsten proposed by Steinbach et al. [27], and the $\underline{N}$H(a) + $\underline{N}$H(a) pathway analogous to the easy combination of $\underline{C}H_2$(a) and $\underline{C}H_2$(a), while the difficult combination of $\underline{N}$(a) and $\underline{N}$(a) analogous to the difficult recombination of $\underline{C}$(a) and $\underline{O}$(a) in syngas reactions on metal surfaces.

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