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Adsorbed NH_x species on Pt(111) and Pt(100) surfaces studied by the semi-empirical method of interacting bonds

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The properties of the adsorbed NH_x species ($x = 0, 1, 2, 3$) on platinum(111) and (100)-(1×1) single-crystal planes are studied by the semi-empirical method of interacting bonds. Both surfaces reveal similar features. The adsorbed species NH and NH_2 are stable on the surface, and stable $NH_{3(ads)}$ species cannot form. The $NH_{2(ads)}$ species is favourable in adsorbed hydrogen excess, but lack of the latter results in NH_{ads} becoming dominant. Both NH and NH_2 species are expected to diffuse easily over the surface due to the small difference between their bond strengths to various adsorption sites.

Keywords: platinum single-crystal surfaces, NH_x intermediates, semi-empirical calculations

1. Introduction

The origin and properties of surface intermediates formed in the course of adsorption and sequential reactions in the adsorbed layer are obviously important for understanding the detailed mechanism of heterogeneous catalytic reactions. Recent experimental studies report on the formation and properties of various $NH_{x(ads)}$ species (where $x = 0, 1, 2, 3$) on platinum single-crystal surfaces [1–4]. Thus, the $NO_{ads} + H_{2(gas)}$ reaction on the Pt(100) surface was studied by means of high-resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS) [3]. As found, the intermediate NH_{ads} species form at a low hydrogen exposure of 0.15 L (Langmuir) at room temperature. Upon further hydrogen exposure of up to 4 L, all nitrogen-containing species are removed from the surface. On the other hand, the initially adsorbed hydrogen excess results in formation of the stable $NH_{2(ads)}$ species, which occurs in the course of the $NO_{gas} + H_{ads}$ reaction on the Pt(100)-(1×1) surface at 300 K [4].

It was established that the stable species NH_{ads} and $NH_{2(ads)}$ were found to be the intermediates in the ammonia oxidation reaction on the Pt(111) surface [1]. These particles were also identified on a Pt(111) single-crystal plane after electron bombardment of the molecularly adsorbed ammonia at 100 K [2]. As found, the $NH_{2(ads)}$ species were dominant below room temperature. An increase in temperature resulted in $NH_{2(ads)}$ dissociation such that the NH_{ads} particles became the main surface species in the temperature range 300–400 K. On further heating, the NH_{ads} species dissociated with the following nitrogen desorption. The papers above are useful for fundamental studies of surface reaction mechanisms. Besides, they are of practical interest, because platinum is currently used in catalytic ammonia oxidation and as an active component of the automotive three-way catalyst [5].

In our previous paper we reported on the properties of $NH_{x(ads)}$ species formed on various single-crystal surfaces of Rh studied by the method of interacting bonds (MIB) [6]. It was found that a stable $NH_{3(ads)}$ particle does not form, and formation of NH_{ads} is more favorable in comparison with that of $NH_{2(ads)}$, thus being in line with the known experimental data [7,8]. In the present paper we report on the similar MIB study of Pt(111) and Pt(100)-(1×1) surfaces elucidating the possibility of formation, priority and properties of various $NH_{x(ads)}$ species. In our calculations, x hydrogen atoms of the $NH_{x(ads)}$ particle are set to bind to the nitrogen atom only, but not to surface platinum atoms. The obtained results are consecutively compared to the available experimental data.

2. Theory

The method of interacting bonds considers a certain multi-atomic system as a set of two-center bonds [9]. Each ith bond is characterized by an empirical parameter E_i similar to the well-known bond energy by its nature. Usually E_i depends only on the type of bond-forming atoms. Besides, for each ith bond we introduce a variable bond coefficient ν_i ($0 < \nu_i < 1$), whose value and, thus, contribution of the ith bond to the total energy of the system is characterized by the whole system structure. The interaction (repulsion) between the ith and kth bonds sharing an atom is also allowed for. This interaction is characterized by an empirical parameter Δ_{ik} which depends on the type of the atoms involved in a certain system formation. Atomization energy is written as

$$H_a = \sum_i E_i \nu_i (2 - \nu_i) - \sum_{i>k} \sum \Delta_{ik} \nu_i \nu_k.$$

Bond coefficients ν_i are found from the maximum of the H_a value (energy minimum):

$$\partial H_a/\partial \nu_i = 0.$$

The simplicity of MIB permits one to investigate any complex system of the desired structure without any additional assumptions such as surfaces, interfaces, extended defects of solids, etc. It should be noted that MIB does not deal with electronic properties of a system considered, therefore determination of atomic coordination numbers, bond angles and other similar features of this system is beyond the model action. For proper use of the MIB results, one certainly has to take into account the molecular geometry, valence, steric features and some other properties of the system considered, which were determined theoretically and/or experimentally.

MIB assumes that the parameters used must be reliable for all the considered systems of rather different properties, through one is not always sure of this. Thus one cannot take for granted a high precision of all the calculated values. However, MIB is sure to provide results of high comparative accuracy. This is very useful for examination of various systems in order to establish conditions of their formation, and select favourable structures and determine their relative stability. We tried to use these potentialities of MIB in the present paper. The method was successfully applied to systems of various chemical origins as oxides [9–11], sulfides [12,13], and metals [16], etc.

3. Results and discussion

3.1. Parameter control

Bond parameters used in our calculations (table 1) were determined from reliable experimental data and tested in previous works [9,11,12,14–16], excepting parameter E_{PtN}, because platinum does not form nitrides, and atomic nitrogen states are formed only indirectly on Pt surfaces [1–4]. We used an empirical correlation $E_{\text{MO}} - E_{\text{MN}} \approx 10$ kcal/mol established for transition metals [9,16]. E_{PtO} values for platinum oxides PtO and PtO$_2$ (103 and 99 kcal/mol, respectively) were calculated from the known structure and formation heats [14,15]. The average value of E_{PtO} was 101 kcal/mol, and E_{PtN} was set to 92 kcal/mol, as in the case of Rh [6].

Table 1
Bond parameters used in MIB calculations.

Parameter	Value (kcal/mol)	Way of determination
E_{PtPt}	79.9	From the heat of Pt sublimation [17]
Δ_{Pt}	18.6	From empirical ratio of $E_{\text{PtPt}}/\Delta_{\text{Pt}} = 4.3$ [16]
E_{NH}	139.4	From NH$_3$ atomization heat [17]
Δ_{N}	75.0	[16]
E_{PtO}	99.0	From heat of PtO$_2$ formation [14,15]
	103	From heat of PtO formation [14,15]
E_{PtN}	92.0	From empirical correlation between E_{PtN} and E_{PtO} [16]

In order to test parameter actions, we have estimated nitrogen desorption energy E_{des} as the double value of the N$_{\text{ads}}$ diffusion activation barrier E_{dif} over the Pt(111) surface (due to simultaneous diffusion of two N$_{\text{ads}}$ species to complete N$_2$ desorption). E_{dif} was determined as a minimum difference between formation heats of various neighboring N$_{\text{ads}}$ states (upper line with pictures in table 3). In the present case, E_{dif} corresponds to the consecutive transition of a nitrogen atom from triple- to double-bound state. Table 2 shows that the calculated E_{des} is lower than the experimental value. This is probably caused by the capability of platinum to form the "surface nitride" shown by HREELS [1] and TDS [18]. Therefore, nitrogen atoms should stronger bound to the surface than it was expected from our calculations. It should be noted that an increase in nitrogen coverage on the platinum(111) surface results in formation of a true-adsorbed state [1], whose E_{des} is very close to our value.

One cannot consider similarly the Pt(100) surface, because nitrogen desorption is complicated by simultaneous (1×1) → hex surface reconstruction ([4,20], and references therein). So, it is not clear which surface structure should be considered in calculations. The estimation of E_{des} from T_{des} [22], which was applied for TDS data on nitrogen desorption from the Pt(100) surface [4,19,21] ranges from 23 to 28 kcal/mol, which is close to the Pt(111) characteristics (table 2). According to our calculations, E_{des} is 33.4 kcal/mol for the (100)-(1×1) surface. To our mind, the above parameters are quite reliable. Nevertheless, the extended E_{PtN} interval was considered in order to elucidate the other possibilities.

3.2. Thermodynamic properties of adsorbed NH$_x$ particles

Heats of NH$_{x\text{(ads)}}$ formation from gaseous nitrogen and hydrogen on Pt(111) and Pt(100) surfaces are presented in table 3. According to table 3, $Q_{\text{f,NH}_x}$ depends insignificantly on the coverage. Multiple states are favorable for all species. All N$_{\text{ads}}$ states and NH$_{\text{ads}}$ species form endothermically, and the NH$_{2\text{(ads)}}$ particles form exothermically. Besides, the respective ν_{PtN} bond parameters for NH$_{3\text{(ads)}}$ states considered are negative. This indicates that the stable NH$_{3\text{(ads)}}$ species does not form, because the ν_{PtN} value is actually responsible for the Pt–N bond strength. Of course, this does not preclude the low-temperature ad-

Table 2
Thermal desorption peak maximum T_{des} and activation energy E_{des} for nitrogen desorption from Pt(111) single-crystal surface.

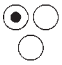
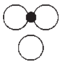
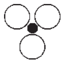
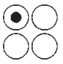
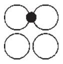
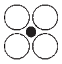
	T_{des} (K)					
	360	420	⩽450	550	450–500	–
E_{des} (kcal/mol)	20.7	24.2	25.9	31.6	25 ± 3	17.2–19.8[a]
Ref.	[1][b]	[1][b]	[2][b]	[2][b]	[19]	[this work]

[a] Smaller and larger values correspond to nitrogen coverages of 1.0 and 0.25 ML, respectively.

[b] E_{des} is estimated from T_{des} according to [22].

Table 3

Heats Q_{f,NH_x} (kcal/mol) of formation of $NH_{x(ads)}$ species (where $x = 0, 1, 2, 3$) on Pt(111) and Pt(100) surfaces at coverage Θ (ML) and various orders of nitrogen atom bonding to the surface according to the reaction $(1/2)N_{2(gas)} + (x/2)H_{2(gas)} \rightarrow NH_{x(ads)} + Q_{f,NH_x}$.

Adsorption state		Surface structure[a]					
		(111)			(100)-(1×1)		
		Pt_1NH_x 	Pt_2NH_x 	Pt_3NH_x 	Pt_1NH_x 	Pt_2NH_x 	Pt_3NH_x 
$Q_{f,N}$	$\Theta = 0.25$	−67.1	−48.7	−38.8	−65.3	−45.9	−29.2
	$\Theta = 1.00$	−66.5	−49.8	−41.2	−64.7	−47.5	−33.4
$Q_{f,NH}$	$\Theta = 0.25$	−17.0	−13.0	−10.6	−16.2	−11.6	−7.2
	$\Theta = 1.00$	−16.9	−13.2	−11.2	−16.0	−12.0	−8.3
Q_{f,NH_2}	$\Theta = 0.25$	2.9	3.1	3.1	3.1	3.3	3.5
	$\Theta = 1.00$	2.9	3.1	3.1	3.1	3.3	3.5
Q_{f,NH_3}	$\Theta = 0.25$	ν(Pt–N) < 0 for every state					
	$\Theta = 1.00$	ν(Pt–N) < 0 for every state					

[a] ○ – surface Pt atom; ● – adsorbed nitrogen or NH_x particle.

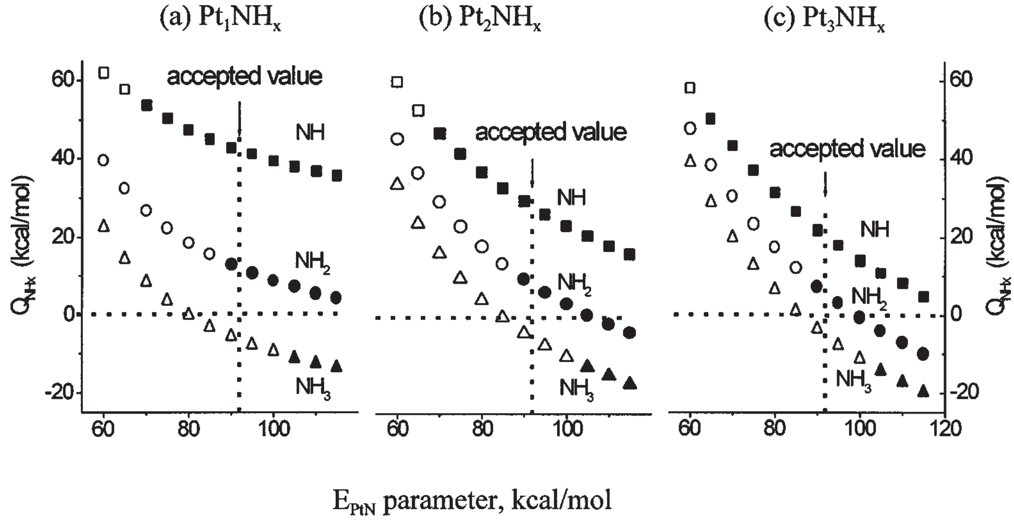


Figure 1. Heats Q_{NH_x} of the sequential steps of N_{ads} hydrogenation in the adsorbed layer on the Pt(111) surface versus bond parameter E_{PtN} according to the reaction $NH_{(x-1)ads} + H_{ads} \rightarrow NH_{x(ads)} + Q_{NH_x}$, where $x = 1, 2, 3$. A nitrogen atom in the $NH_{x(ads)}$ particle is single- (a), double- (b) and triple-bound (c) to the platinum surface, as shown in table 3. Solid and open symbols stand for $\nu_{PtN} > 0$ (the given state may be formed) and $\nu_{PtN} < 0$ (the given state may not be formed), respectively.

sorption of molecular ammonia caused by van der Waals interaction or hydrogen bond formation.

Figures 1 and 2 show the heats of successive steps of the N_{ads} hydrogenation according to the reaction

$$NH_{(x-1)ads} + H_{ads} \rightarrow NH_{x(ads)} + Q_{NH_x}$$

where $x = 1, 2, 3$, and a hydrogen adsorption heat of 16 kcal/mol [23] was accepted for all cases.

The above reaction proceeds if $Q_{NH_x} > 0$ and $\nu_{ij} > 0$ only, where ν_{ij} is the bond coefficient between any ith and jth atoms within the whole system considered. In figures 1 and 2, the lower and higher limits of the E_{PtN} interval correspond to weak Ag–N and strong V–N or Mo–N bonds, respectively [16]. Regarding the strength of nitrogen atom bonding, platinum takes a medium position between Ag and V or Mo, thus one can follow the parametric regions of existence of various NH_x species. An increase in the E_{PtN} parameter is accompanied by a decrease in formation heats of $NH_{x(ads)}$ species and an increase in ν_{PtN} (not shown in figures 1 and 2). This negative ν_{PtN} prohibits formation of the respective particles at low E_{PtN}. The first step of the N_{ads} hydrogenation is the most exothermical. A step of the $NH_{2(ads)}$ formation is also possible at the accepted parameter E_{PtN}. For the multiple bonding of adsorbed species to the surface, we have determined heats of the following successive transformations in the adsorbed layer at the current value of $E_{PtN} = 92$ kcal/mol:

$$(1/2)N_{2(gas)} \rightarrow N_{ads}$$

$$-38.8 \text{ kcal Pt(111)} \quad -29.2 \text{ kcal Pt(100)} \tag{1}$$

$$N_{ads} + (1/2)H_{2(gas)} \rightleftharpoons NH_{ads}$$

$$+28.2 \text{ kcal Pt(111)} \quad +22.0 \text{ kcal Pt(100)} \tag{2}$$

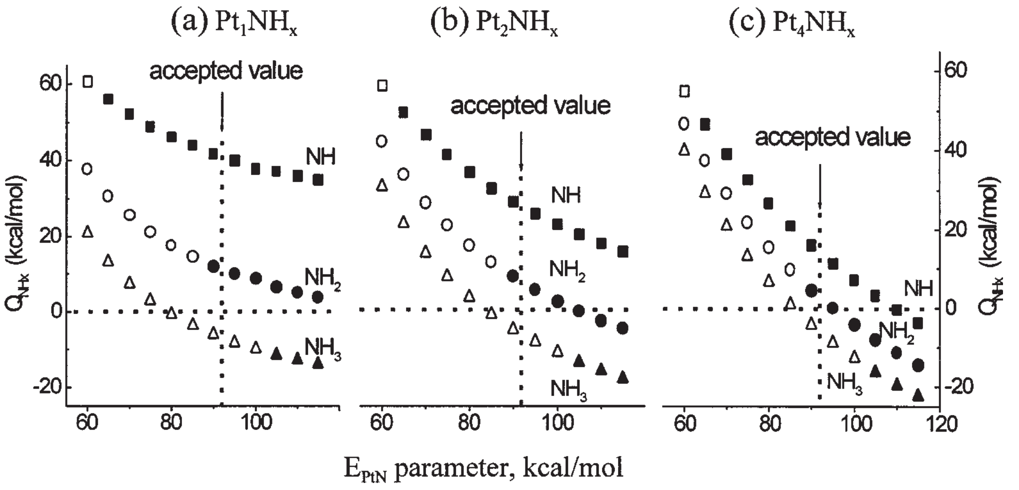


Figure 2. Heats Q_{NH_x} of the sequential steps of N_{ads} hydrogenation in the adsorbed layer on the Pt(100) surface versus bond parameter E_{PtN} according to the reaction $NH_{(x-1)ads} + H_{ads} \rightarrow NH_{x(ads)} + Q_{NH_x}$, where $x = 1, 2, 3$. A nitrogen atom in the $NH_{x(ads)}$ particle is single- (a), double- (b) and triple-bound (c) to the platinum surface, as shown in table 3. Solid and open symbols stand for $\nu_{PtN} > 0$ (the given state may be formed) and $\nu_{PtN} < 0$ (the given state may not be formed), respectively.

$$NH_{ads} + (1/2)H_{2(gas)} \rightleftharpoons NH_{2(ads)}$$
$$+13.7 \text{ kcalPt(111)} \quad +10.7 \text{ kcal Pt(100)} \qquad (3)$$
$$2NH_{ads} \rightarrow N_{2(ads)} + H_{2(gas)}$$
$$+21.2 \text{ kcal Pt(111)} \quad +14.4 \text{ kcal Pt(100)} \qquad (3a)$$
$$NH_{2(ads)} + (1/2)H_{2(gas)} \rightarrow NH_{3(gas)}$$
$$+7.9 \text{ kcal Pt(111)} \quad +7.5 \text{ kcal Pt(100)} \qquad (4)$$
$$2NH_{2(ads)} \rightarrow N_{2(gas)} + 2H_{2(gas)}$$
$$-6.2 \text{ kcal Pt(111)} \quad -7.0 \text{ kcal Pt(100)} \qquad (4a)$$

Therefore, formation of both stable species NH_{ads} and $NH_{2(ads)}$ is possible, but a $NH_{2(ads)}$ particle prefers to form in hydrogen excess because of the exothermicity of steps (2) and (3) in the forward direction. This agrees with the experimental data presented in [1–4]. Hydrogen removal from the surface, which may result from an increase in the temperature, should shift reaction (3) to the left. In this case the NH_{ads} particle becomes dominant on the surface. Ammonia formation (step (4)) and/or recombination of $NH_{2(ads)}$ particles (step (4a)) may accompany this process. Further hydrogen removal from the surface may also shift step (2) to the left. As a result, the N_{ads} species should predominate on the surface. Besides, step (3a) of NH_{ads} recombination is also possible. These peculiarities of the adsorbed layer, resulting from the present MIB calculations, are very close to the experimental observations and conclusions of [2] concerning the properties of the NH_x species on the Pt(111) single-crystal surface. Moreover, the TD spectra presented in [2,18] show that H_2 and N_2 desorption proceed simultaneously in the temperature range 450–500 K, though the authors did not emphasize this observation. This is probably caused by the NH_{ads} recombination above.

Figures 3 and 4 show the heat of $NH_{x(ads)}$ species formation from gaseous N_2 and H_2 calculated for the region around the accepted parameter E_{PtN}. Note that heats of single-, double-, and multiple-bound particles formation differ insignificantly on both surfaces. This probably indicates that the values of the respective diffusion activation barriers are rather low, and the adsorbed NH and NH_2 species can easily move over the surface, thus, providing the removal of strongly bound N_{ads} states from the surface in the presence of hydrogen via intermediate formation of NH_{ads} and/or $NH_{2(ads)}$ species. These particles may mutually diffuse to take part in the combination reactions (3a), (4a) or leave the surface via ammonia formation (step (4)). This pathway was probably realized in [21], where atomic nitrogen was removed from a Pt(100) surface in the presence of H_2 even at room temperature.

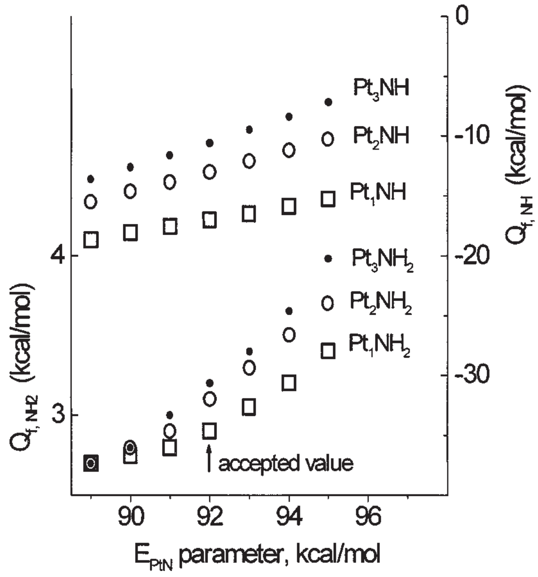


Figure 3. Heat Q_{f,NH_x} of $NH_{x(ads)}$ species formation on the Pt(111) surface versus E_{PtN} parameter at various orders of nitrogen atom bonding to the surface (see designations in table 3) according to the reaction $(1/2)N_{2(gas)} + (x/2)H_{2(gas)} \rightarrow NH_{x(ads)} + Q_{f,NH_x}$, where $x = 1, 2$; calculations were performed for a coverage of 0.25 ML.

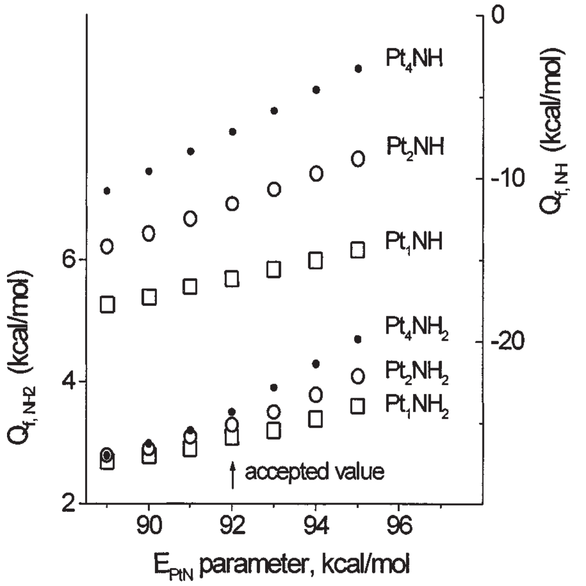


Figure 4. Heat $Q_{\mathrm{f,NH}_x}$ of NH$_{x\mathrm{(ads)}}$ species formation on the Pt(100) surface versus E_{PtN} parameter at various orders of nitrogen atom bonding to the surface (see designations in table 3) according to the reaction $(1/2)\mathrm{N}_{2(\mathrm{gas})} + (x/2)\mathrm{H}_{2(\mathrm{gas})} \rightarrow \mathrm{NH}_{x(\mathrm{ads})} + Q_{\mathrm{f,NH}_x}$, where $x = 1, 2$; calculations were performed for a coverage of 0.25 ML.

4. Conclusions

We have analyzed the properties of $\mathrm{NH}_{x(\mathrm{ads})}$ species on Pt(111) and Pt(100)-(1×1) single-crystal planes by the semi-empirical method of interacting bonds. The platinum surfaces revealed similar features. In particular:

(i) In contrast to Rh, both species $\mathrm{NH}_{\mathrm{ads}}$ and $\mathrm{NH}_{2(\mathrm{ads})}$ are stable on the platinum surface, whereas the stable $\mathrm{NH}_{3(\mathrm{ads})}$ particle cannot be formed.

(ii) The $\mathrm{NH}_{2(\mathrm{ads})}$ species is favorable in an excess of adsorbed hydrogen. The lack of the latter results in the $\mathrm{NH}_{\mathrm{ads}}$ particle becoming dominant.

(iii) $\mathrm{NH}_{\mathrm{ads}}$ and $\mathrm{NH}_{2(\mathrm{ads})}$ species are expected to diffuse easily over the surface. Their removal from the surface may proceed via the following pathways:

  - successive dissociation followed by nitrogen desorption (in the lack of hydrogen);
  - full hydrogenation and ammonia desorption (in hydrogen excess);
  - recombination reaction with simultaneous H_2 and N_2 desorption.

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