The Role of NH_n Species in Oscillation Phenomena in the NO + H_2 Reaction on Noble Metal Surfaces: Semi-Empirical Calculations

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Abstract

The semi-empirical Method of Interacting Bonds was used in the present work to clarify the mechanism of the title process. Various single crystal planes of Pt, Rh, Ir, Fe, and Re were examined with respect to the stability of the adsorbed NH_n species (n = 0, 1, 2, 3); to the reactivity of NH_n (n = 0, 1, 2) species towards adsorbed hydrogen atoms; and to the possibility of proceeding the combination reactions between two NH or two NH_2 particles resulting in the formation of gaseous H_2 and N_2 molecules. All the surfaces studied were found to form readily the stable NH species. The principal difference between Pt, Rh, Ir single crystal planes, on which the reaction exhibits rate oscillations, and Fe, Re surfaces, which do not show an oscillatory behavior, is that the combination reaction of NH species can easily proceed in the former case, but this reaction is not allowed thermodynamically on the latter surfaces. This result is consistent with an earlier suggested mechanism for the oscillatory behavior that attributes the surface wave propagation to the intermediate formation of NH species. Stable NH_2 species can be formed on Re and Fe surfaces, whereas the noble metal surfaces can form weakly stable NH_2 particles at the very edge of their existence region. The combination reaction between two NH_2 species is endothermic in all cases.

INTRODUCTION

The nature 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. In the case of the NO reduction reactions, they are also of practical interest since, in particular platinum and rhodium, are currently used in catalytic ammonia oxidation, and as active component of the automotive three-way catalyst [1, 2]. A series of experimental studies report on the formation and properties of various $NH_{n\ ads}$ species (where n = 0, 1, 2, 3) on platinum single crystal surfaces [3–7]. Thus, the intermediate NH_{ads} species were found to form in the reaction of $H_{2\ gas}$ + NO_{ads} on the Pt(100) surface at hydrogen exposure of 0.15 L (Langmuir) at 300 K. An increase in the hydrogen exposure to 4 L removes all nitrogen containing species from the surface [7]. It was shown that NH_{ads}, and $NH_{2\ ads}$ species are intermediates in the ammonia oxidation reaction on the Pt(111), and Pt(100) surfaces [3, 4]. These species were also identified on the Pt(111) single crystal plane after electron bombardment of molecularly adsorbed ammonia at 100 K [5]. The authors reported that $NH_{2\ ads}$ species were dominant below room temperature. Dissociation of these species occurs in the temperature range 300–400 K, and NH_{ads} become the main surface species.

There is also a number of reliable experimental data, which clearly demonstrate the formation of stable NH_{ads} and $NH_{2\ ads}$ species on various single crystal surfaces of Rh [8], Ir [9, 10], Fe [11–13], and Re [14].

Several noble metal surfaces are known to reveal a nonlinear kinetic behavior in the reaction of NO + H_2. More specifically, such a behavior was reported for several platinum, rhodium, and iridium single crystal surfaces as well as for monocrystalline tips [15–18]. Processes such as surface explosions, surface wave propagation, and oscillations in reaction rate display these nonlinear phenomena. The proposed mechanisms usually involve a reversible surface reconstruction, interaction in the adlayer or an autocatalytic increase in formation of vacancies in the course of reaction [19]. The combination of two N_{ads} species was considered as the major stage of $N_{2\ gas}$ formation. Besides that, the reversible formation of intermediate NH_n species followed by combination reaction $2NH_{n\ ads} \rightarrow N_{2\ gas} + nH_{2\ gas}$ was proposed to play an important role in oscillation phenomena [16, 20–22].

In our previous papers we reported on the properties of $NH_{n\ ads}$ species formed on various single crystal surfaces of Rh and Pt studied by the Method of Interacting Bonds (MIB) [21, 22]. It was found that stable $NH_{3\ ads}$ species are not formed, and formation of NH_{ads} is more favorable in comparison with that of $NH_{2\ ads}$, thus being in line with known experimental data [16, 23].

In the present work we report on a similar comparative MIB study of Pt(100)-(1×1), Rh(111), Rh(100), FCC Fe(111), and Re(0001) single crystal planes in order to find out the regularity in properties of various NH_n species. Iron and rhenium do not reveal non-linear behavior in the NO + H_2 reaction, but they are known to form various NH_n species. The aim of including the latter metals in the present work is to elucidate the part of intermediate NH_n species in the title process.

In our calculations, n hydrogen atoms of the $NH_{n\ ads}$ particle are set to bind to the nitrogen atom only, but not to surface metal atoms. We present in this work data only corresponding to the strongly bound species, *i. e.* the N atom of NH_n is triply bound to surfaces with C_{3v} symmetry, and fourfold bound to surfaces with C_{4v} symmetry. The Rh(533) single crystal surface is known to reveal oscillations in the reaction rate of the NO + H_2 reaction [15]. The Rh(111), and Rh(100) planes were considered in the present work as a components of the Rh(533) plane since the latest can be represented as 4(111) × 1(100). The results obtained are compared with available experimental data.

THEORY

The method of interacting bonds considers a certain multiatomic system as a set of two-center bonds [24]. Each i-th 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 i-th bond we introduce a variable bond coefficient ν_i ($0 < \nu_i < 1$), whose value and, thus, contribution of the i-th bond to the total energy of the system is characterized by the whole system structure. The interaction (repulsion) between the i-th and k-th bonds sharing an atom is also allowed for. This interaction is characterized by an empirical parameter Δ_{ik} that depends on the type of the atoms involved into a certain system formation. Atomization energy is written as:

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

Bond coefficients ν_i are found from the maximum of the H_a value (energy minimum): $\partial H_\mathrm{a} / \partial \nu_i = 0$.

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 the electronic properties of the system considered. Therefore, determination of atomic coordination numbers, bond angles, and other similar features of this system are beyond the model action. For proper use of the MIB results, one certainly has to account for the molecular geometry, valence, steric features and some other properties of the system considered, which were determined theoretically and/or experimentally. The bond parameters used in the present work are listed in Table 1. All E_{MM} parameters were determined from corresponding evaporation enthalpies. All Δ_M parameters were estimated from the empirical ratio $E_{MM}/\Delta_M = 4.3$ [25].

TABLE 1

Bond parameters used in MIB calculations, kJ/mol

Atom	E_{MM}	Δ_M	E_{MN}	E_{NH}	Δ_N
Fe	246.34[a]	57.29	405.0[b]	583.25 [21]	313.8 [25]
Re [26]	456.6	106.2	555.3		
Rh [21]	333.0	77.4	405.8		
Ir	392.9	91.4	453.1[c]		
Pt [22]	334.3	77.7	384.9		

[a] E_{FeFe} is determined from the sublimation heat of γ-Fe.

[b] E_{FeN} is determined from the atomization heat of Fe_4N.

[c] E_{IrN} is determined from the empirical correlation between E_{IrN} and E_{IrO} [25], that is determined from the formation enthalpies of IrO and IrO_3.

MIB assumes that the parameters used must be reliable for all the systems considered having rather different properties, though this is not always sure. Thus one cannot take for granted a high precision of all the calculated values. However, MIB is able to provide results with high comparative accuracy. This is very useful for examination of various systems in order to establish the conditions of their formation, and select favorable 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 such as oxides [24, 27, 28], sulphides [29, 30], and metals [25], *etc*.

RESULTS AND DISCUSSION

The following key points concerning NH_{ads} and $NH_{2\ ads}$ species, have been considered for a set of single crystal surfaces in order to clarify the title process:

1. The stability characteristics of adsorbed species. A given $NH_{n,ads}$ species is forbidden to form if any of its bond parameters is negative, *i. e.* $\nu_{MN} < 0$ and/or $\nu_{NH} < 0$; the particle is stable if $\nu_{MN} > 0.1$ and $\nu_{NH} > 0.1$; the particle is weakly stable for intermediate values of bond parameters.

2. The heat of formation Q_1 in the adsorbed layer according to the reactions:

$$N_{ads} + H_{ads} \rightarrow NH_{ads} + Q_1 \quad (1)$$

$$NH_{ads} + H_{ads} \rightarrow NH_{2\ ads} + Q_1 \quad (2)$$

The formation of a given species is allowed if $Q_1 \geq 0$. The value of Q_1 was determined as: $Q_1 = Q_{NH} - Q_N - Q_H$ (for NH_{ads} formation) and as: $Q_1 = Q_{NH_2} - Q_{NH} - Q_H$ (for $NH_{2\ ads}$ formation), where Q_H stands for the half of the experimental heat of hydrogen adsorption whose values are presented in Table 2. It is assumed to be independent of coverage for a given surface; Q_N, Q_{NH}, Q_{NH_2} stand for the calculated heat of formation of the respective species:

$$1/2N_{2\ gas} \rightarrow N_{ads} + Q_N \quad (3a)$$

$$1/2N_{2\ gas} + 1/2H_{2\ gas} \rightarrow NH_{ads} + Q_{NH} \quad (3b)$$

$$1/2N_{2\ gas} + H_{2\ gas} \rightarrow NH_{2\ ads} + Q_{NH_2} \quad (3c)$$

3. The possibility of the combination reaction to proceed according to equations:

$$2NH_{ads} \rightarrow N_{2\ gas} + H_{2\ gas} + Q_2 \quad (4)$$

$$2NH_{2\ ads} \rightarrow N_{2\ gas} + 2H_{2\ gas} + Q_2 \quad (5)$$

A given reaction is supposed to be allowed if the heat of reaction $Q_2 \geq 0$.

Reactions (4) and (5) are considered as a possible contribution to the total reaction rate,

TABLE 2

The heat of H_2 adsorption on the metal surfaces examined

Heat of NH_2 adsorption	Fe(110)	Re(0001)	Rh	Ir(110)	Pt
Q_{ads}, kJ/mol	83.0 [35]	83.4 [34]	77.8 [31, 32]	83.2 [36]	66.9 [33]

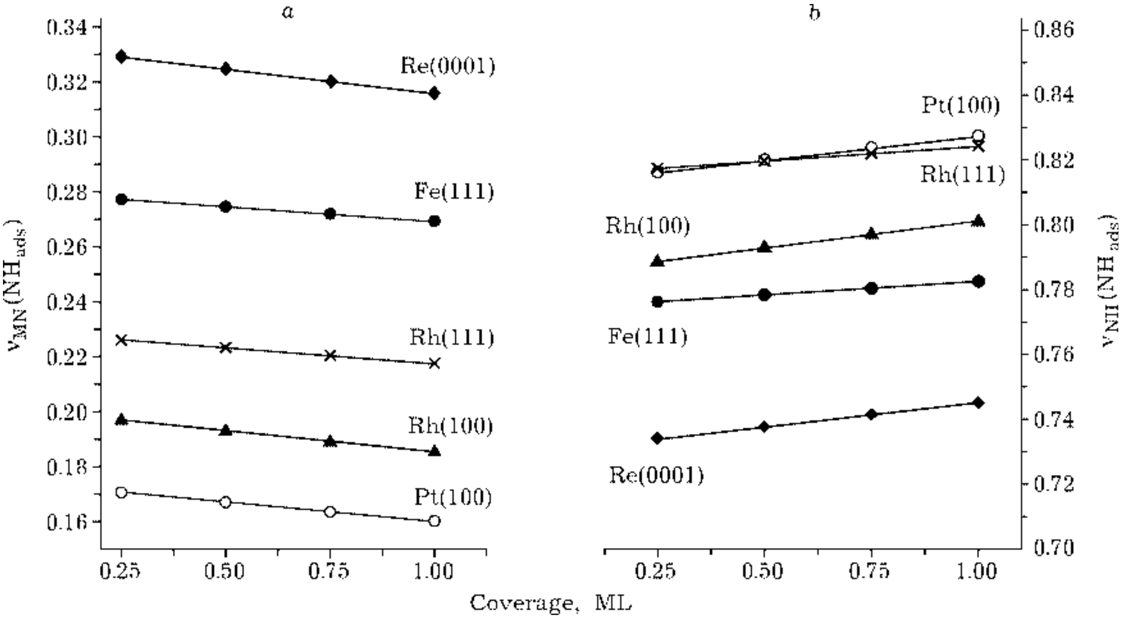

Fig. 1. The bond coefficient ν_{MN} (*a*) and ν_{NH} (*b*) of NH species adsorbed on different single crystal planes as a function of coverage.

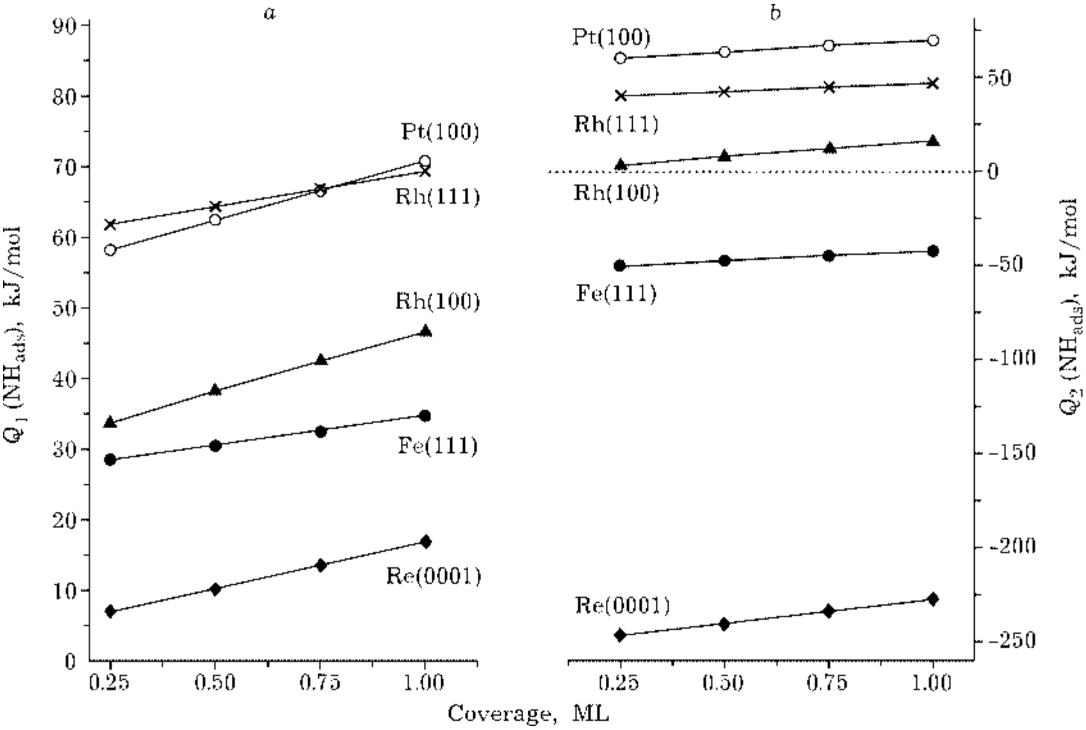

Fig. 2. Heat of formation (*a*) by eq. (1) and heat of combination reaction (*b*) by eq. (4) of NH species on different single crystal planes as a function of coverage.

which is mainly determined by ordinary reactions of $2N_{ads} \rightarrow N_{2\ gas}$.

Figures 1 and 2 show the results of the calculations concerning adsorbed NH species on a set of single crystal surfaces at various coverages. In all cases NH_{ads} species are quite stable as shown in Fig. 1. The ν_{MN} bond coefficient (*i. e.* M–N bond strength) slightly decreases and the ν_{NH} bond coefficient (*i. e.* N–H bond strength) slightly increases as the coverage rises. The ν_{NH} bond coefficient of the adsorbed NH species even exceeds the

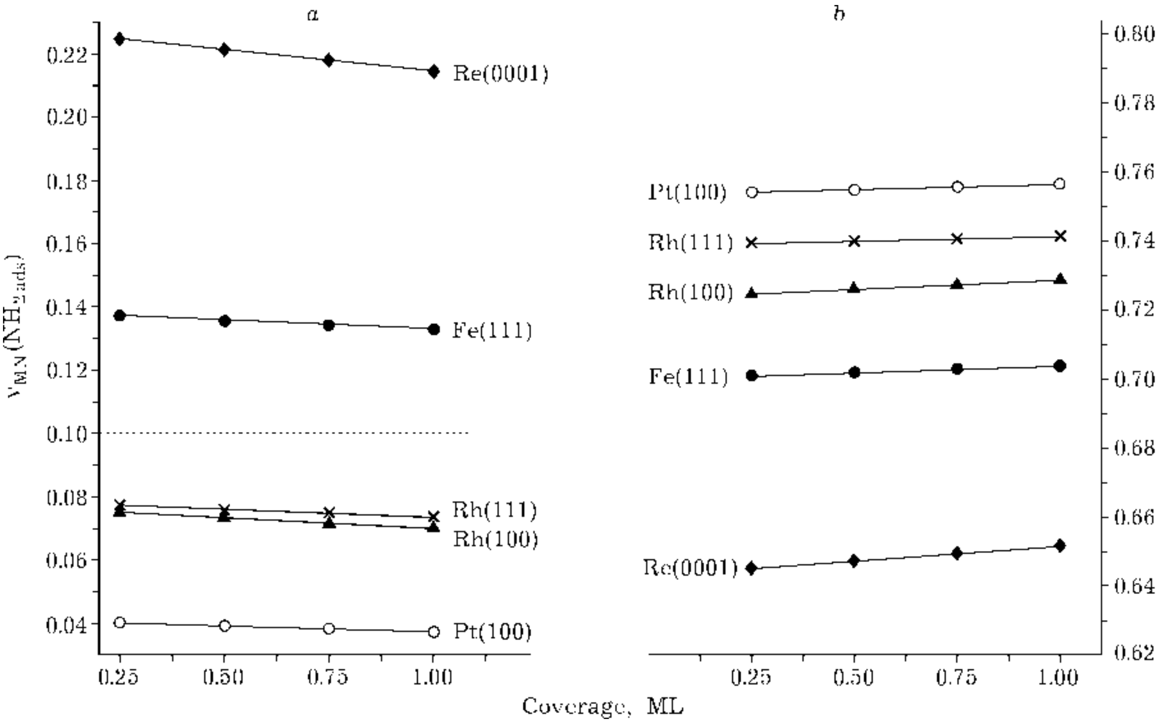

Fig. 3. The bond coefficient ν_{MN} (*a*) and ν_{NH} (*b*) of NH$_2$ species adsorbed on different single crystal planes as a function of coverage.

value of ν_{NH} = 0.65 corresponding to the gaseous NH$_3$ molecule.

Figure 2, *a* shows that NH$_{ads}$ species readily form in the adsorbed layer. It means that not N$_{ads}$, but NH$_{ads}$ species are favorable in the presence of adsorbed hydrogen at low temperature. An excess of H$_2$ in the reaction mixture NO + H$_2$ corresponds to the experimental conditions required for sustained oscillations in the reaction rate [15, 17, 18].

Figure 2, *b* illustrates an important feature of NH$_{ads}$ species. Namely, the combination reaction is allowed on those surfaces ($Q_2 > 0$), which reveal oscillatory behavior, and it is forbidden for surfaces ($Q_2 < 0$), which do not reveal oscillations. Besides that, the heat of the combination reaction increases (*i. e.* Gibbs energy change decreases) as the coverage rises. This result is in line with another experimental characteristic of oscillation phenomena; because a certain critical coverage is always necessary to start the regular surface wave propagation.

Figure 3 demonstrates the stability of adsorbed NH$_2$ particles. The same dependence on coverage was found in the case of the NH species: the M–N bond strength slightly decreases, and the N–H bond strength slightly increases as the coverage rises. Re(0001) and Fe(111) surfaces exhibit a rather high n_{MN} value, *i. e.* strong M–N bond, whereas the value on the noble metal surfaces corresponds to weakly bound NH$_2$ particles ($\nu_{MN} < 0.1$, this boundary value is marked by the dotted line in Fig. 3, *a*). The N–H bond strength of NH$_2$ species is weaker than that of NH species.

Figure 4 shows the thermodynamic properties of NH$_2$. In contrast to NH species, the formation of NH$_2$ species in the adsorbed layer by eq. (2) is favorable for Pt(100) and Rh(111) surfaces only, and the combination reaction by eq. (5) is not allowed for all surfaces.

Even a brief analysis of the data presented in Figs. 1–4 evidences that our calculation points to a common regularity in the row of examined surfaces:

Pt(100)-(1×1), Rh(111), Rh(100), Fe(111),
Re(0001) (6)

In this order:

– the heat of formation of NH and NH$_2$ species (eqs. (1) and (2)) decreases;

– the heat of the respective combination reaction (eqs. (4) and (5)) decreases;

– the N–H bond strength decreases;

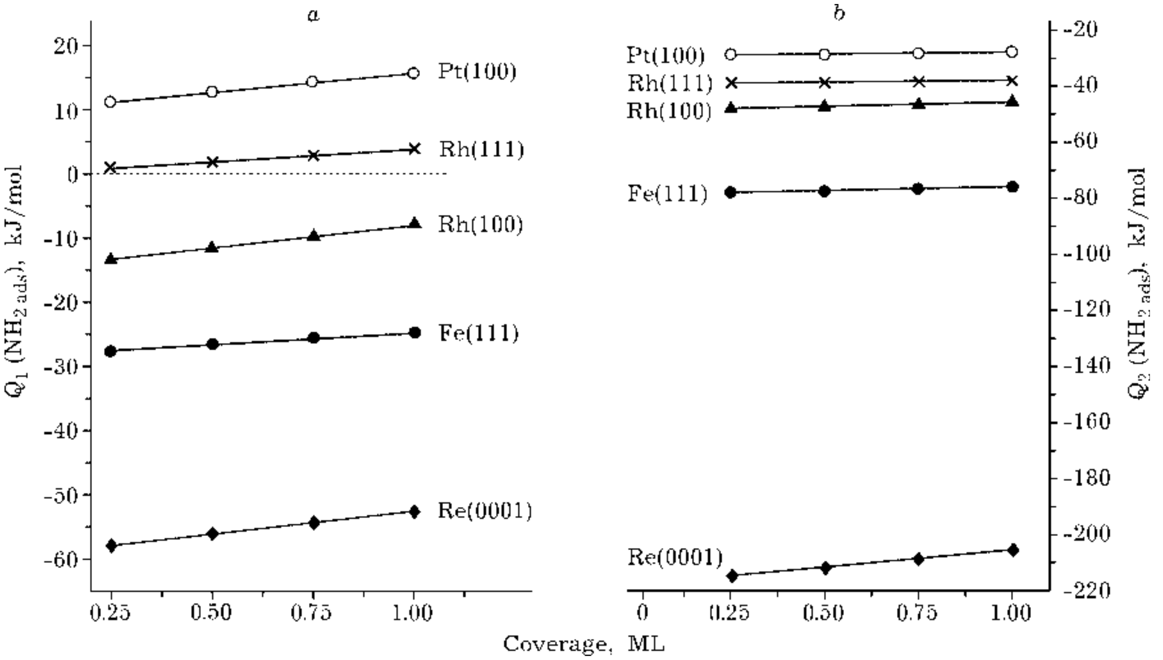

Fig. 4. Heat of formation (*a*) by eq. (2), and heat of the combination reaction (*b*) by eq. (5) of NH_2 species on different single crystal planes as a function of coverage.

– the M–N bond strength increases.

Table 3 is designed to find out those characteristics among the collection of experimental and theoretical data, which may be responsible for the title process.

Table 3 shows that the line No. 1 (oscillatory behavior) agrees completely with line No. 7 (NH combination), and only partly with line No. 8 (NH_2 formation). The formation of adsorbed NH_2 species cannot be responsible for the oscillatory behavior, because the stability of $NH_{2\,ads}$ (line No. 9) reveals an opposite behaviour. Moreover, the combination reaction of $NH_{2\,ads}$ (line No. 10) is not allowed thermodynamically.

In contrast to that, the reaction of NH combination can be most probably responsible for the oscillatory behavior. Indeed, N_{ads} species can be readily formed (line No. 2 in Table 3), and adsorbed oxygen atoms can be readily removed from the surface by an excess of hydrogen in the reaction mixture. Both the further formation of NH particles in the adsorbed layer, and the combination reaction are sub-

TABLE 3

Combined experimental and calculated data on single crystal surfaces

Line No.	Characteristic	Pt(100)-(1×1)	Rh(111)/(100)	Fe(111) FCC	Re(0001)
1	Oscillatory Behaviour*	+	+	–	–
2	NO dissociation*	+	+	+	+
3	Surface reconstruction*	+	–	–	–
4	Availability of NH_n species*	+	+	+	+
5	NH formation	+	+	+	+
6	NH stability	+	+	+	+
7	NH combination	+	+	–	–
8	NH_2 formation	+	+/–	–	–
9	NH_2 stability	–	–	+	+
10	NH_2 combination	–	–	–	–

*Experimental data.

stantially exothermic as shown in Fig. 2. In addition, the intermediate NH species are rather stable as demonstrated in Fig. 1.

A preliminary consideration of the Ir(110) single crystal surface shows that the (1×1) structure should be inactive in oscillations since its properties are close to that of Fe(111). On the contrary, the properties of the Ir(110)-(1×2) surface are close to that of Rh(111). It means that the reconstructed iridium surface should be active in oscillations. It agrees with the experimental observations, which demonstrate that non-linear kinetic behavior of the Ir(110) surface in the NO + H_2 reaction proceeds under experimental conditions at which the surface is reconstructed [17, 37].

The data presented in Figs. 1–4 concern only the strongly bound species (M_3NH_x or M_4NH_x) as the most favorable reaction intermediates, if any. Consideration of other species like M_2NH_x, and M_1NH_x (*i. e.* particles bonded with two, and one surface atoms M, respectively) revealed the following pattern for all the same surfaces as above. For both NH and NH_2 particles, each of examined parameters enhances substantially on decrease of the number of bonding to the surface in the row M_3NH/M_4NH, M_2NH, and M_1NH. It namely concerns M–N bond strength, N–H bond strength, heat of NH (and NH_2) formation in the adsorbed layer, and heat of the respective combination reaction. The heat of NH_2 combination reaction remains negative in all cases. Thus, the decrease of number of bonds between NH_n particle and surface enhances the role of NH species as a possible intermediate in oscillation phenomena.

CONCLUSIONS

1. The semi-empirical Method of Interacting Bonds was used to analyze the properties of adsorbed NH_n species on a set of single crystal planes of transition metals. A regularity is established for the following surfaces examined: Pt(100)-(1×1), Rh(111), Rh(100), Fe(111), Re(0001). In this order the properties of NH and NH_2 species change: the heat of formation, the heat of the respective combination reactions, and the N–H bond strength decrease, whereas the M–N bond strength increases.

2. The principal difference between Pt, Rh, single crystal planes, on which the reaction of NO + H_2 exhibits rate oscillations, and Fe, Re surfaces, which do not show an oscillatory behavior, is that the combination reaction of NH species can easily proceed in the former case, but it is not allowed on the latter surfaces. Thus, the combination reaction between two adsorbed NH species can be most probably responsible for the oscillatory behavior of the considered noble metal single crystal planes. This result is consistent with an earlier suggested mechanism for the oscillatory behavior, which attributes the surface wave propagation to the intermediate formation of NH species.

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