Catalysis Letters Vol. 86, Nos. 1–3, March 2003 (© 2003)

Semi-empirical calculations on the stability and reactivity of NH_x species on metal surfaces

A.R. Cholach [a], N.N. Bulgakov [a], and B.E. Nieuwenhuys [b],*

[a] *Boreskov Institute of Catalysis, Pr. Akad. Lavrentieva 5, 630090 Novosibirsk, Russia*
[b] *Leiden Institute of Chemistry, PO Box 9502, 2300 RA Leiden, The Netherlands*

Received 19 September 2002; accepted 13 November 2002

The semi-empirical method of interacting bonds was used to elucidate the mechanism of oscillation phenomena in the $NO + H_2$ reaction on metal surfaces. Basic single-crystal planes of Pt, Rh, Ir, Fe, Ru, and Re were examined with respect to the stability of adsorbed NH_n species ($n = 0, 1, 2, 3$); to the reactivity of NH_n ($n = 0, 1, 2$) species toward adsorbed hydrogen atoms; and to the possibility of combination reactions between two NH or two NH_2 species resulting in the formation of gaseous N_2 molecules. All studied surfaces were found to form readily stable NH species. The principal difference between Pt, Rh, and Ir single-crystal planes exhibiting reaction rate oscillations, and Fe, Ru, and Re surfaces, which do not show an oscillatory behavior, is that the combination reaction of NH species can easily proceed in the former case, whereas this reaction is not allowed thermodynamically in the latter. This result is consistent with an earlier suggested model that attributes the oscillatory surface wave propagation to the intermediate formation of NH species.

Stable NH_2 species can be formed on Ru, Re, and Fe surfaces, whereas the noble metal surfaces of Pt, Rh, and Ir can only form weakly stable NH_2 species at the very edge of their existence region. The combination reaction between two NH_2 species is endothermic in all cases.

KEY WORDS: noble metals; single-crystal surfaces; $NO + H_2$ reaction; oscillation phenomena; NH_x intermediates; semi-empirical calculations.

1. Introduction

The nature and properties of surface intermediates formed in the course of adsorption and reactions in adsorbed layers 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 the catalytic oxidation of ammonia, and as active components of the automotive three-way catalyst [1,2]. A number of papers report the formation and properties of various $NH_{n,\mathrm{ads}}$ 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 $H_{2,\mathrm{gas}} + NO_{\mathrm{ads}}$ on the Pt(100) surface at an exposure to hydrogen 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 $NH_{2,\mathrm{ads}}$ 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 surface after electron bombardment of molecularly adsorbed ammonia at 100 K [5]. The authors reported that $NH_{2,\mathrm{ads}}$ species were dominant below room temperature. Dissociation of these species occurs in the temperature range 300–400 K, and NH_{ads} becomes the main surface species.

There are also reliable experimental data that evidently demonstrate the formation of stable NH_{ads} and $NH_{2,\mathrm{ads}}$ species on various single-crystal surfaces of Rh [8], Ir [9,10], Fe [11–13], Ru [14], and Re [15].

Several noble metal surfaces are known to reveal a non-linear 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 [16–19]. Processes such as surface explosions, surface wave propagation, and oscillations in the reaction rate are examples of these non-linear 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 [20]. The combination reaction between two N_{ads} species is being considered as the main source of $N_{2,\mathrm{gas}}$ formation. Besides that, the reversible formation of intermediate NH_n species, and combination reactions of these species resulting in $N_{2,\mathrm{gas}}$ desorption were proposed to play an important role in oscillation phenomena [17,21–23].

In previous papers we reported on the properties of $NH_{n,\mathrm{ads}}$ species formed on various single-crystal surfaces of Rh and Pt studied by the method of

---

* To whom correspondence should be addressed.
E-mail: b.nieuew@chem.leidenuniv.nl

1011-372X/03/0300-0009/0

interacting bonds (MIB) [22,23]. It was found that stable $NH_{3,ads}$ species are not formed, and formation of NH_{ads} is more favorable in comparison with $NH_{2,ads}$, which is in agreement with known experimental data [17,24].

In the present work we report on a similar comparative MIB study of Pt(100)-(1 × 1), Rh(111), Rh(100), Ir(110)-(1 × 1), Ir(110)-(1 × 2), FCC Fe(111), Ru(0001), and Re(0001) single-crystal planes in order to determine a possible regularity in the properties of the various NH_n species. As shown experimentally, all examined surfaces can form readily stable NH_n species. Nevertheless, the noble metals Pt, Rh, and Ir exhibit nonlinear behavior in the $NO + H_2$ reaction, whereas Fe, Ru, and Re do not [20]. The aim of including the latter metals in the present work is to elucidate the role of intermediate NH_n species in oscillation phenomena in the $NO + H_2$ reaction on noble metal surfaces.

In our calculations, n hydrogen atoms of the $NH_{n,ads}$ species are set to bind to the nitrogen atom only, and not to surface metal atoms. We present in this work only data 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 [16]. The Rh(111) and Rh(100) planes were considered in this work as components of the Rh(533) plane since the latter can be represented as 4(111) × 1(100). The results obtained are compared with available experimental data.

Different coverages of adsorbed NH_n species were considered in the present work, in particular coverages of 0.25, 0.5, and 1 ML (monolayer) corresponding to the p(2 × 2), c(2 × 2), and p(1 × 1) structures of the adsorbed layer, respectively. A coverage of 0.75 ML corresponds to a p(2 × 2) structure of vacant sites. Our previous calculations show that the adlayer properties of 0.25 ML coverage are very close to those of 0 ML (one single particle at an infinite surface).

2. Theory

The method of interacting bonds considers a certain multi-atomic system as a set of two-center bonds [25]. 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 v_i $(0 < v_i < 1)$, 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}, which depends on the type of the atoms involved in the formation of a certain system. The atomization energy is written as:

Table 1
Bond parameters used in MIB calculations (kJ/mol)

	E_{MM}	Δ_M	E_{MN}	E_{NH}	Δ_N
Fe	246.34	57.29	405.0	583.25 [22]	313.8 [27]
Re	456.6	106.2	555.3		
Ru	381.1	88.6	520.4		
Rh [22]	333.0	77.4	405.8		
Ir	392.9	91.4	453.1		
Pt [23]	334.3	77.7	384.9		

$$H_a = \sum_i E_i v_i (2 - v_i) - \sum_{i>k}\sum \Delta_{ik} v_i v_k$$

The bond coefficients v_i are found from the maximum of the H_a value (energy minimum):

$$\partial H_a / \partial v_i = 0$$

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 scope of the model. 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 are 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 the corresponding evaporation enthalpies [26]. All Δ_M parameters were estimated from the empirical ratio $E_{MM}/\Delta_M = 4.3$ [27]. Parameters E_{FeFe} and E_{FeN} were determined from the heat of sublimation of γ-Fe and the heat of atomization of Fe_4N, respectively [26,28]. The parameter E_{IrN} was determined from the empirical correlation between E_{IrN} and E_{IrO} [27], and the latter was determined from the enthalpies of formation of IrO and IrO_3 [29]. The parameters E_{ReN} and E_{RuN} were determined from the respective Re–N [30] and Ru–N [31] bond energies.

MIB assumes that the parameters used must be reliable for all the systems considered having rather different properties, although this is not always the case. 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 the examination of various systems in order to establish the conditions of their formation, to select favorable structures, and to 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 [25,32,33], sulfides [34,35], metals [27], etc.

3. 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:

- 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. $\upsilon_{MN} < 0$ and/or $\upsilon_{NH} < 0$; the particle is stable if $\upsilon_{MN} > 0.1$, and $\upsilon_{NH} > 0.1$; the particle is weakly stable for intermediate values of bond parameters $0.1 > \upsilon_{MN}$, $\upsilon_{NH} > 0$.
- The heat of formation Q_1 in the adsorbed layer according to the reactions

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

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

The formation of a given species is allowed if $Q_1 \geq 0$. The value of Q_1 was determined as

$$Q_1 = Q_{NH} - Q_N - Q_H \quad \text{(for } NH_{ads} \text{ formation)}$$

and as

$$Q_1 = Q_{NH_2} - Q_{NH} - Q_H \quad \text{(for } NH_{2,ads} \text{ formation)}$$

where Q_H represents half of the experimental heat of hydrogen adsorption whose values are presented in table 2, which is assumed to be independent of coverage for a given surface; and Q_N, Q_{NH}, and Q_{NH_2} represent the calculated heat of formation of the respective species:

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

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

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

Table 2
The heat of H_2 adsorption (Q_{ads}) on the examined metal surfaces (kJ/mol)

Re(0001)	Ru(0001)	Fe(110)	Rh	Ir(110)	Pt
83.4 [36]	87.0 [37]	83.0 [38]	77.8 [39,40]	83.2 [41]	66.9 [42]

- The possibility of the combination reaction to proceed according to the equations

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

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

A given reaction is supposed to be allowed if the heat of reaction $Q_2 \geq 0$. It should be noted that reactions (4) and (5) are considered as a possible contribution to the total rate of N_2 formation, which is mainly determined by

$$2N_{ads} \rightarrow N_{2,gas}$$

Figures 1 and 2 show the results of calculations related to the properties of NH_{ads} species on the surfaces

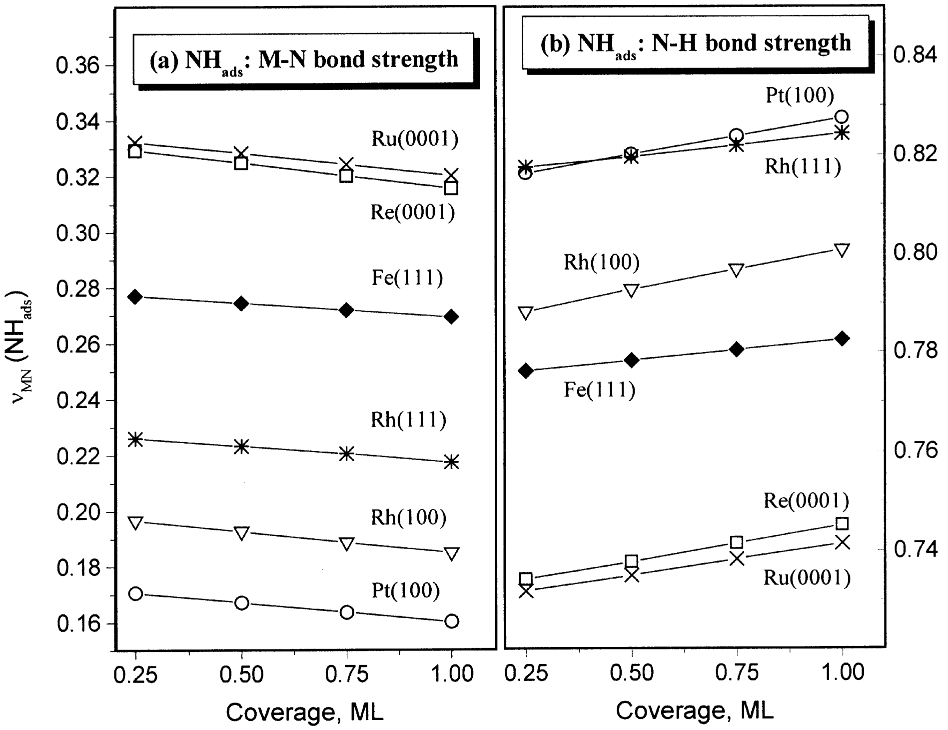

Figure 1. The bond coefficient υ_{MN} (a) and υ_{NH} (b) of NH species adsorbed on the studied single-crystal planes as a function of coverage. M = Pt(100)-(1 × 1), open circles; Rh(111), asterisks; Rh(100), open triangles; Fe(111), filled diamonds; Ru(0001), crosses; Re(0001), open squares.

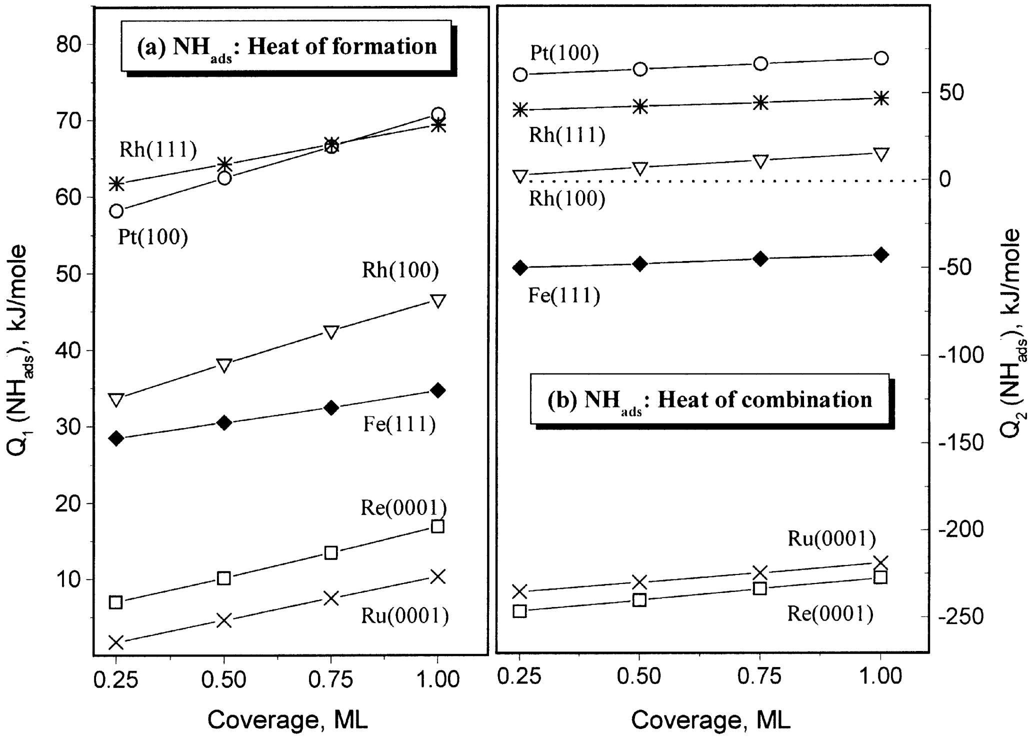

Figure 2. The heat of formation (a) by equation (1) and the heat of combination reaction (b) by equation (4) of NH species on the studied single-crystal planes as a function of coverage. The dotted line at $Q_2 = 0$ displays the boundary between allowed (above zero) and forbidden (below zero) energy regions of the combination reaction to proceed.

examined as a function of coverage. In all cases NH_{ads} species are quite stable as evidenced from figure 1. The υ_{MN} bond coefficient (i.e. M–N bond strength) slightly decreases, and the υ_{NH} bond coefficient (i.e. N–H bond strength) slightly increases as the coverage increases. The υ_{NH} bond coefficient of the adsorbed NH species even exceeds the value of $\upsilon_{NH} = 0.65$ corresponding to the gaseous NH_3 molecule.

Figure 2(a) shows that NH_{ads} species readily form in the adsorbed layer. This 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 [16,18,19].

Figure 2(b) illustrates an important feature of NH_{ads} species. Namely, the combination reaction is allowed on those surfaces that reveal oscillatory behavior, and it is forbidden for surfaces that do not reveal oscillations. Besides that, the heat of the combination reaction increases (i.e. Gibbs energy change decreases) as the coverage increases. This result may be in agreement 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 species. The same dependence on coverage was found as 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 increases. Figure 3(a) shows that Re(0001), Ru(0001), and Fe(111) surfaces exhibit a rather high υ_{MN} value, i.e. a strong M–N bond, whereas the υ_{MN} value on the noble metal surfaces corresponds to weakly bound NH_2 particles ($\upsilon_{MN} < 0.1$; this boundary is marked with the dotted line in figure 3(a)). The N–H bond strength of NH_2 species is weaker than that of NH species as evidenced from the comparison of figures 1(b) and 3(b).

Figure 4 shows thermodynamic properties of NH_2. In contrast to NH species, the formation of NH_2 species in the adsorbed layer by equation (2) is slightly favorable for Pt(100) and Rh(111) surfaces only, and the combination reaction by equation (5) is strongly endothermic on all surfaces.

Even a brief analysis of the data presented in figures 1–4 shows that our calculations point to a common regularity in the series of examined surfaces:

$$\text{Pt(100)-}(1 \times 1), \text{Rh(111)}, \text{Rh(100)}, \text{Fe(111)}, \text{Ru(0001)}, \text{Re(0001)} \quad (6)$$

In this order:

- the heat of formation of NH and NH_2 species (equations (1) and (2)) decreases;
- the heat of the respective combination reaction (equations (4) and (5)) decreases;
- the N–H bond strength decreases;
- the M–N bond strength increases.

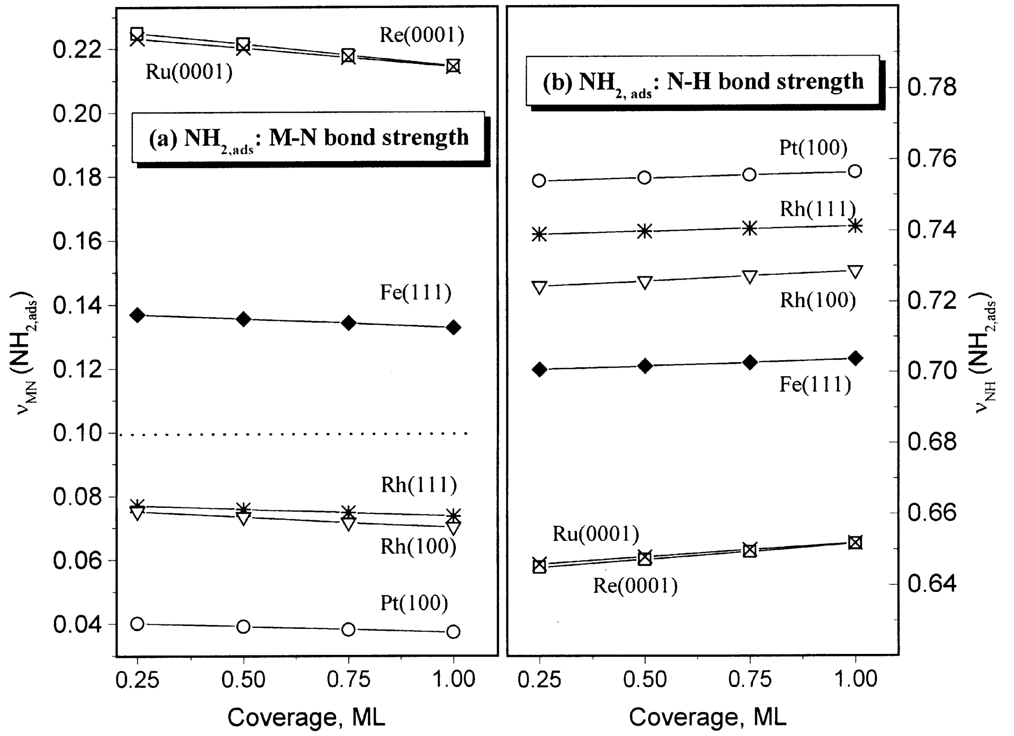

Figure 3. The bond coefficient v_{MN} (a) and v_{NH} (b) of NH_2 species adsorbed on the studied single-crystal planes as a function of coverage. M = Pt(100)-(1 × 1), open circles; Rh(111), asterisks; Rh(100), open triangles; Fe(111), filled diamonds; Ru(0001), crosses; Re(0001), open squares. The dotted line at $v_{MN} = 0.1$ displays the boundary between strong (above 0.1) and weak (below 0.1) M–N bond strength of $NH_{2,ads}$ species.

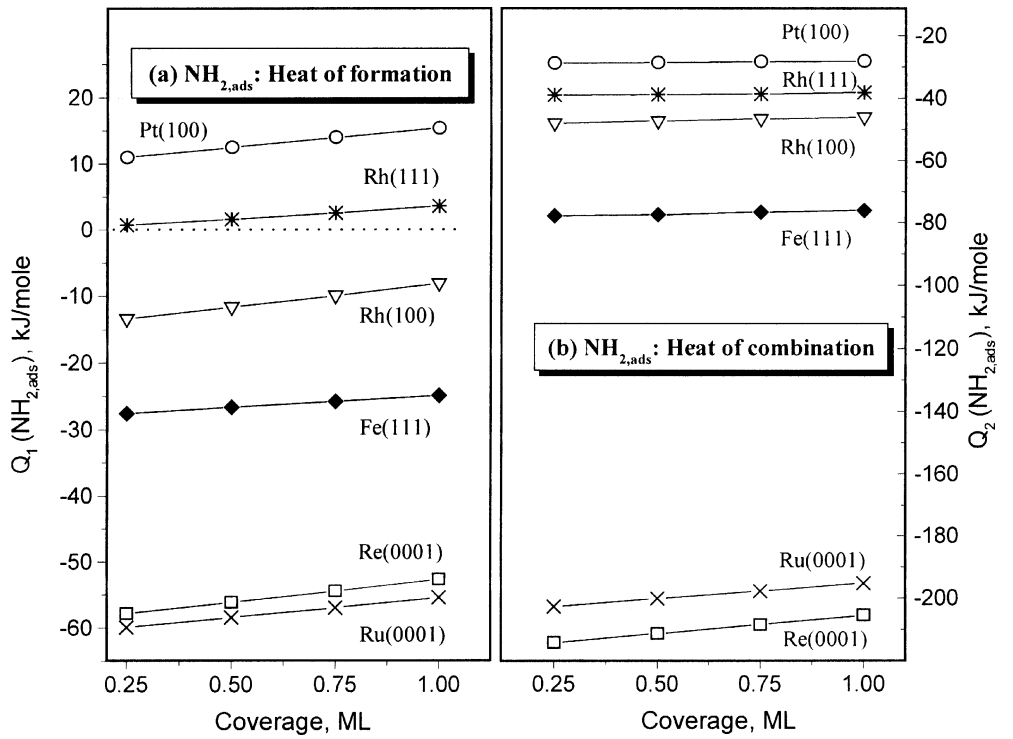

Figure 4. The heat of formation (a) by equation (2) and the heat of combination reaction (b) by equation (5) of NH_2 species on the studied single-crystal planes as a function of coverage. The dotted line at $Q_1 = 0$ displays the boundary between allowed (above zero) and forbidden (below zero) energy regions of the formation reaction to proceed.

Table 3
Combined experimental (*) and calculated data on single-crystal surfaces

No.	Characteristic	Pt(100)-(1 × 1)	Rh(111)/(100)	Fe(111)-FCC	Ru(0001)	Re(0001)
1	*Oscillatory behavior	+	+	−	−	−
2	*NO dissociation	+	+	+	+	+
3	*Surface reconstruction	+	−	−	−	−
4	*Availability of NH$_x$ species	+	+	+	+	+
5	NH formation	+	+	+	+	+
6	NH stability	+	+	+	+	+
7	NH combination	+	+	−	−	−
8	NH$_2$ formation	+	+/−	−	−	−
9	NH$_2$ stability	−	−	+	+	+
10	NH$_2$ combination	−	−	−	−	−

The properties of Ru(0001) and Re(0001) single-crystal planes are actually very close to each other, as can be seen from figures 1–4.

Table 3 is designed to determine those characteristics among the collection of experimental and theoretical data that may be responsible for oscillation phenomena in the $NO + H_2$ reaction on metal surfaces. Table 3 shows that line 1 (oscillatory behavior) agrees completely with line 7 (NH combination), and only partly with line 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 9) reveals an opposite behavior. Moreover, the combination reaction of $NH_{2,ads}$ (line 10) is not allowed thermodynamically.

In contrast to that, the reaction of NH combination (line 7) is most probably responsible for the oscillatory behavior. We note the drastic difference between oscillating and non-oscillating surfaces in this respect accounting for the rather rough ordinate scale in figure 2(a). Indeed, N_{ads} species can be readily formed (line 2) and adsorbed oxygen atoms can be readily removed from the noble metal surface by an excess of hydrogen in the reaction mixture. Both the further formation of NH species in the adsorbed layer and the combination reaction are substantially exothermic as shown in figure 2. In addition, the intermediate NH species are rather stable as evidenced from figure 1.

The capability of the adsorbed NH species of undergoing the combination reaction on the Ir(110)

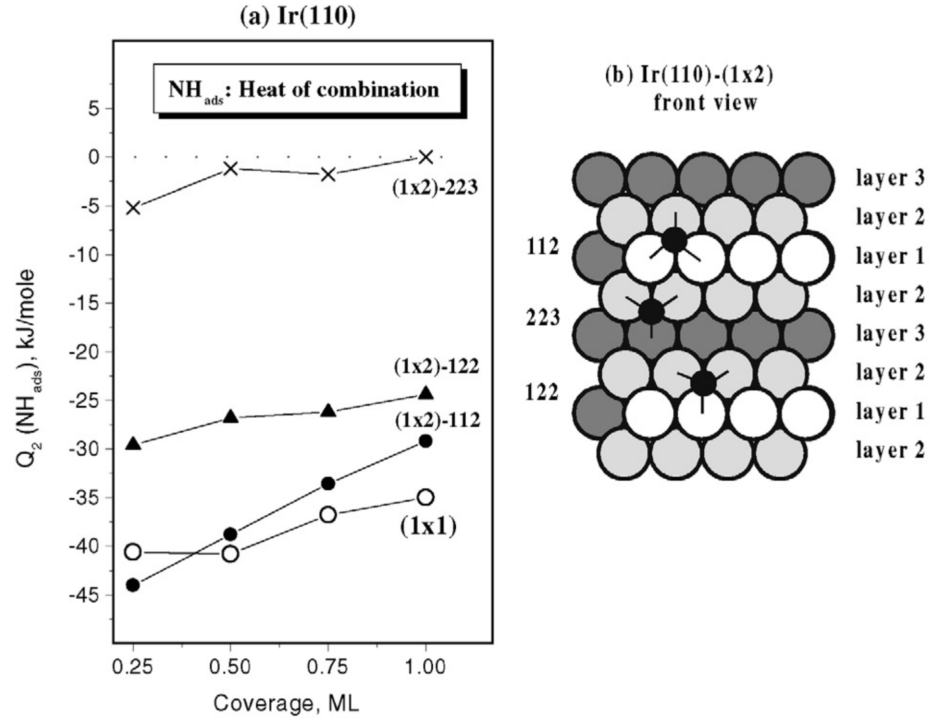

Figure 5. (a) The heat of combination of NH species (equation (4)) adsorbed on the Ir(110)-(1 × 1) surface (open circles), and adsorbed on different sites of the Ir(110)-(1 × 2) surface, as a function of coverage. (b) Schematic illustration of the different triply bound NH_{ads} states (small black circles) corresponding to (a). For details of designations, see text.

Table 4
The relative M–N bond strength (υ_{NM}) and the relative N–H bond strength (υ_{NH}) of $NH_{3,ads}$ species on examined surfaces at coverage of 0.25 ML

	Ru(0001)	Re(0001)	Fe(111)	Rh(100)	Rh(111)	Ir(110)-(1 × 1)[a]	Ir(110)-(1 × 2)[a]	Pt(100)
υ_{NM}	0.1370	0.1431	0.0218	−0.0282	−0.0461	0.0572 −0.0482	0.0419 −0.0379	−0.0719
υ_{NH}	0.5783	0.5751	0.6388	0.6699	0.6744	0.6386	0.6362	0.7005

[a] There are two kinds of Ir–N bonds due to the peculiarity of the structure of the (110) plane as demonstrated in figure 5(a) (curve (1 × 2)-223) and in figure 5(b). Namely, two larger υ_{NM} values correspond to two bonds of the N atom with Ir atoms of the second layer, and one smaller (negative) υ_{NM} value corresponds to one bond of the N atom with an Ir atom of the third layer.

single-crystal plane is presented in figure 5. The top curve designated as (1 × 2)-223 in figure 5(a) corresponds to an ordered layer of triply bound NH species on the Ir(110)-(1 × 2) surface; and every NH species in these layers has two bonds with the nearest Ir atoms of the second layer, and one bond with an Ir atom of the third layer, as demonstrated in figure 5(b). A similar explanation concerns the other curves in figure 5(a). Namely, the curve (1 × 2)-122 corresponds to NH species bound to one Ir atom of the first layer and to two Ir atoms of the second layer, and the curve (1 × 2)-112 corresponds to NH species bound to two Ir atoms of the first layer and to one Ir atom of the second layer. Curve (1 × 1) represents the properties of the unreconstructed Ir(110)-(1 × 1) surface.

Figure 5(a) shows that the Ir(110)-(1 × 1) single-crystal plane is inactive in the combination reaction (4) of NH species, but the surface reconstruction essentially modifies this quality. It is clearly seen that the deeper the NH_{ads} particle is located on the Ir(110)-(1 × 2) surface the higher is the exothermicity of the combination reaction. The value of Q_2 amounts to zero at high coverage (curve (1 × 2)-223 in figure 5(a)). Actually the presence of grooves on the reconstructed Ir(110)-(1 × 2) surface allows the combination reaction to proceed. Comparison of figures 2(b) and 5(a) shows that the properties of the deeply located NH_{ads} layer on the Ir(110)-(1 × 2) surface are close to those on the Rh(100) surface, and the properties of the Ir(110)-(1 × 1) surface are close to those of the Fe(111) one. On the basis of this consideration the reconstructed (1 × 2) iridium surface should be active in oscillations, whereas the (1 × 1) surface should not. This agrees with the experimental observations, which demonstrate that the 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 [18,43].

Table 4 displays the properties of $NH_{3,ads}$ species on the surfaces examined to complete our investigation. These species are stable enough on Ru and Re single-crystal planes, weakly stable on Fe, and not stable on noble metal surfaces according to their respective υ_{NM} values. An increasing coverage results in a further decrease of the M–N bond strength, and a slight increase of the N–H bond strength, such as in the case of the NH and NH_2 species shown in figures 1 and 3. The combination reaction of $NH_{3,ads}$ similar to equations (4) and (5) is endothermic in all cases. It is very unlikely that $NH_{3,ads}$ species have a substantial role in the oscillation phenomena in the $NO + H_2$ reaction on metal surfaces.

The data presented in figures 1–5 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 species, each of the examined parameters are substantially enhanced on a decrease of the number of bonds to the surface in the series M_3NH/M_4NH, M_2NH, and M_1NH: the 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 reactions. The heat of the NH_2 combination reaction remains negative in all cases. Thus, a decrease of a number of bonds between a NH_n species and the surface enhances the role of NH species as a possible intermediate in oscillation phenomena.

4. Conclusions

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), Ru(0001), Re(0001). In this order the properties of NH and NH_2 species change: the heat of formation, the heat of the respective combination reaction, and the N–H bond strength decrease, whereas the M–N bond strength increases.

The principal difference between Pt, Rh, and Ir single-crystal planes exhibiting oscillations in the rate of the $NO + H_2$ reaction, and Fe, Ru, and Re surfaces, which do not show an oscillatory behavior, is that the combination reaction of NH species can easily proceed in the former case, whereas it is substantially endothermic in the latter. Thus, the combination reaction between two adsorbed NH species is most probably responsible for the oscillatory behavior of the considered noble metal single-crystal planes.

Acknowledgment

The authors appreciate the financial support from INTAS99-01882.

References

[1] K.C. Taylor, in: *Automotive Catalytic Converters* (Springer, Berlin, 1984).
[2] B.E. Nieuwenhuys, Adv. Catal. 44 (1999) 259.
[3] W.D. Mieher and W. Ho, Surf. Sci. 322 (1995) 151.
[4] J.M. Bradley, A. Hopkinson and D.A. King, J. Phys. Chem. 99 (1995) 17032.
[5] Y.-M. Sun, D. Sloan, H. Ihm and J.M. White, J. Vac. Sci. Technol. A 14 (1996) 1516.
[6] D.Yu. Zemlyanov, M.Yu. Smirnov, V.V. Gorodetskii and J.H. Block, Surf. Sci. 329 (1995) 61.
[7] D.Yu. Zemlyanov, M.Yu. Smirnov and V.V. Gorodetskii, Surf. Sci. 391 (1997) 37.
[8] A. Vavere and R.S. Hansen, J. Catal. 69 (1981) 158.
[9] B.J. Wood and H. Wise, J. Catal. 39 (1975) 471.
[10] V.V. Gorodetskii and V.A. Sobyanin, in: *Proc. 7th ICC* (Kadansha, Tokyo, 1981) p. 566.
[11] K. Kishi and M.W. Roberts, Surf. Sci. 62 (1977) 252.
[12] M. Grunze, F. Bozso, G. Ertl and M. Weiss, Appl. Surf. Sci. 1 (1978) 241.
[13] M. Drechsler, H. Hoinkes, H. Kaarmann, H.W. Wilsch, G. Ertl and M. Weiss, Appl. Surf. Sci. 3 (1979) 217.
[14] K. Yacoby, H. Dietrich and G. Ertl, Appl. Surf. Sci. 121/122 (1997) 558.
[15] Y. Fukuda, F. Honda and J.W. Rabalais, Surf. Sci. 99 (1980) 289.
[16] N.M.H. Janssen, B.E. Nieuwenhuys, M. Ikai, K. Tanaka and A.R. Cholach, Surf. Sci. 319 (1994) L29.
[17] A.R. Cholach, M.F.H. van Tol and B.E. Nieuwenhuys, Surf. Sci. 320 (1994) 281.
[18] C.A. de Wolf, B.E. Nieuwenhuys, A. Sasahara, K. Tanaka, M.M. Slinko and M.Yu. Smirnov, Surf. Sci. 411 (1998) L904.
[19] J. Siera, P.D. Cobden and B.E. Nieuwenhuys, Catal. Lett. 10 (1991) 335.
[20] C.A. de Wolf and B.E. Nieuwenhuys, Catal. Today 70 (2001) 287.
[21] A.G. Makeev, M.M. Slinko, N.N.H. Janssen, P.D. Cobden and B.E. Nieuwenhuys, J. Chem. Phys. 105 (1996) 7210.
[22] A.R. Cholach and N.N. Bulgakov, Catal. Lett. 48 (1997) 191.
[23] A.R. Cholach and N.N. Bulgakov, Catal. Lett. 58 (1999) 183.
[24] M.F.H. van Tol, A. Gielbert and B.E. Nieuwenhuys, Catal. Lett. 16 (1992) 297.
[25] N.N. Bulgakov, Yu.A. Borisov and V.V. Popovskii, Kinet. Katal. 14 (1973) 395 (in Russian).
[26] D.R. Lide (ed.), *Handbook of Chemistry and Physics*, 73rd edition (CRC Press, 1992) ch. 5.
[27] A.I. Boldyrev, V.I. Avdeev, N.N. Bulgakov and I.I. Zakharov, Kinet. Katal. 17 (1976) 706 (in Russian).
[28] B.P. Nikol'skii (ed.), *Handbook of Chemistry* (Moscow, 1962) p. 789 (in Russian).
[29] V.P. Glushko (ed.), *Handbook on Thermal Constants of Substances*, Vol. 6 (Moscow, 1973) p. 194 (in Russian).
[30] N.E. Henriksen and G.D. Billing, Surf. Sci. 227 (1990) 224.
[31] H. Shi, K. Jacobi and G. Ertl, J. Chem. Phys. 99 (1993) 9248.
[32] N.N. Bulgakov, V.Yu. Aleksandrov and V.V. Popovskii, React. Kinet. Catal. Lett. 4 (1976) 473.
[33] N.N. Bulgakov, V.Yu. Aleksandrov and V.V. Popovskii, React. Kinet. Catal. Lett. 8 (1978) 53, 59, 65.
[34] Yu.I. Yermakov, A.N. Startsev, V.A. Burmistrov, O.N. Shumilo and N.N. Bulgakov, Appl. Catal. 18 (1985) 33.
[35] N.N. Bulgakov and A.N. Startsev, Mendeleev Commun. 1 (1991) 98.
[36] R. Ducros, M. Housley, G. Piquard and M. Alnot, Surf. Sci. 109 (1981) 235.
[37] P. Feulner and D. Menzel, Surf. Sci. 154 (1985) 465.
[38] K. Yoshida, Japan J. Appl. Phys. 19 (1980) 1873.
[39] V.V. Gorodetskii, B.E. Nieuwenhuys, V.M. Sachtler and G.K. Boreskov, Surf. Sci. 108 (1981) 225.
[40] A. Crucq, G. Lienard, L. Degols and A. Frennet, Appl. Surf. Sci. 17 (1983) 79.
[41] J.M. Derochette, Surf. Sci. 118 (1982) 145.
[42] B. Hellsing, B. Kasemo and V.P. Zhdanov, J. Catal. 132 (1991) 210.
[43] D.E. Ibbotson, T.S. Wittrig and W.H. Weinberg, Surf. Sci. 111 (1981) 149.