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# Resonant active sites in catalytic ammonia synthesis: A structural model

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ABSTRACT

Adsorption sites $M_n$ consisted of $n$ adjacent atoms $M$, each bound to the adsorbed species, are considered within a realistic model. The sum of bonds $\Sigma$ lost by atoms in a site in comparison with the bulk atoms was used for evaluation of the local surface imperfection, while the reaction enthalpy at that site was used as a measure of activity. The comparative study of $M_n$ sites ($n = 1$–5) at basal planes of Pt, Rh, Ir, Fe, Re and Ru with respect to heat of $N_2$ dissociative adsorption $Q_N$ and heat of $N_{ad} + H_{ad} \rightarrow NH_{ad}$ reaction $Q_{\underline{NH}}$ was performed using semi-empirical calculations. Linear $Q_N(\Sigma)$ increase and $Q_{\underline{NH}}(\Sigma)$ decrease allowed to specify the resonant $\Sigma$ for each surface in catalytic ammonia synthesis at equilibrium $N_{ad}$ coverage. Optimal $\Sigma$ are realizable for $Ru_2$, $Re_2$ and $Ir_4$ only, whereas other centers meet steric inhibition or unreal crystal structure. Relative activity of the most active sites in proportion $5.0 \times 10^{-5}$: $4.5 \times 10^{-3}$: 1: 2.5: 3.0: 1080: 2270 for a sequence of $Pt_4$, $Rh_4$, $Fe_4$(fcc), $Ir_4$, $Fe_{2-5}$(bcc), $Ru_2$, $Re_2$, respectively, is in agreement with relevant experimental data. Similar approach can be applied to other adsorption or catalytic processes exhibiting structure sensitivity.

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## 1. Introduction

Surface imperfections of different origin, chemical nature and morphology play a complex role in heterogeneous catalysis. They become the active sites for target reactions, inhibitor accumulation, traps for charged species, etc. [1,2]. The presence of defects may be the necessary condition of adsorption and different catalytic processes [3,4]. The relevance of the structure gap between idealized models and real catalysts with various surface defects was evident for decades, but the systematic studies of such surfaces have begun only after reasonable understanding of the model systems [5]. Defects may influence the reactivity through geometric or electronic effects related to the specific surface structure that affects the coverage and stabilizes the activated states [6]. The number of experimental and theoretical evidence of extremely high reactivity of the certain defects on transition metal surfaces grows continuously [7,8]. For example, the CO molecule cannot dissociate on the Rh(111) surface, while the presence of steps on this surface decrease the activation barrier by ~120 kJ/mol and enable the C–O bond breaking [7,9]. Steps decrease energy barriers for $N_2$ and NO dissociation by 100 kJ/mol in comparison with the most close-packed surfaces of Ru, Fe, Mo or Pd [7]. The site stabilization effect 50–80 kJ/mol at edges and corners of Pt nanoparticles against the Pt(111) plane were reported for $CH_n$ species [10]. CO oxidation and $O_2$ reduction on the Pt(111) in the alkaline media serve as a model of defect-favored and terrace-favored reaction, respectively [6]. Catalytic NO reduction by $H_2$ on noble metal surfaces has received much attention due to its importance for the automobile exhaust control [11]. The study of NO + $H_2$ reaction on the Rh tip using the Field Emission Microscopy revealed that surface defects and probably grain boundaries are responsible for initiation of the chemical waves caused by the large difference in N–Rh bond strength and, hence, in reactivity [12]. The CO + $O_2$ reaction on Pt(110) and Pt(210) is actually governed by the structural defects [13], while the point and extended defects can become active sites for adsorption, surface reactions and cluster nucleation [14]. The importance of defects is indicated by frequent variation of activity with particle size. This fact has led to a conclusion about existence of structure-sensitive reactions [15–17].

Most catalytic surfaces are not uniformly active. They exhibit activity only at the sites with special arrangement or chemical composition of the surface atoms [15], and thus the concept of active sites is fundamental to the heterogeneous catalysis [8,18]. The distribution of nitrogen atoms on the Ru(0001) surface after nitric oxide dissociation allowed to establish that the active sites are formed by the low coordinated, top metal atoms of atomic steps. The results demonstrate the complex manner, in which the structure of a catalytic surface determines the activity of the catalyst, and confirm the active sites concept [8]. It turns out that the substantial part of basic field concepts has been discovered during the development of the Haber–Bosch process, and so the history of catalytic ammonia synthesis can be regarded as a capsule version of the heterogeneous catalysis history [19,20]. Among iron single crystals, Fe (111) and Fe (211) possess the highest activity, which has been attributed to "$C_7$ sites" corresponding to 7-coordinated Fe atom in the second layer [17,21]. Similar Ru sites exhibited no specific catalytic activity in the ammonia synthesis, and enhanced activities of certain Ru crystal faces were related to their comparatively large

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**Table 1**
Empirical parameters and heats of $H_2$ adsorption ($Q_{H2}$) used in calculations, kJ/mol.

|  | $Q(H_2)$ | $E_{MM}$ | $\Delta_M$ | $E_{MN}$ | $E_{NH}$ | $\Delta_N$ |
|---|---|---|---|---|---|---|
| Pt | 67.0 | 334.3 | 77.7 | 384.9 | 596.4 | 313.8 |
| Rh | 77.8 | 333.0 | 77.4 | 405.8 |  |  |
| Ir | 83.2 | 392.9 | 91.4 | 453.1 |  |  |
| Ru | 87.0 | 381.1 | 88.6 | 520.4 |  |  |
| Re | 83.4 | 456.6 | 106.2 | 555.3 |  |  |
| Fe bcc | 83.0 | 273.5 | 63.6 | 404.5 |  |  |
| Fe fcc | 83.0 | 246.3 | 57.3 | 404.5 |  |  |

roughness and openness [16]. The subsequent papers reported the responsibility of $B_5$ sites for high activity of Ru-based catalysts in $NH_3$ synthesis [22–24]. However, the exact nature of active sites as well as the mechanism of their catalytic promotion remains a matter of speculation [8].

Specific behavior of surface imperfections is usually interpreted qualitatively. According to the general rule, the step sites exhibit enhanced catalytic activity if a metal surface is not highly active and vice versa, the role of undercoordinated sites is much less essential in case of highly reactive metals [5]. The Taylor' "Theory of the Catalytic Surface" emphasizes the important role of defect sites formed by atoms with "unsaturated valencies" [25]. This concept has been successfully developed by means of experimental and theoretical methods [4,8,18], and our contribution is as follows: we suggest that the *total* valence unsaturation (in comparison with bulk atoms) is the measure of an adsorption site imperfection [26]. The importance of this topic and the lack of quantitative data have encouraged the present study of the surface defects on basal planes of transition and noble metals with respect to the $N_2$ dissociative adsorption and $N_{ad} + H_{ad} \rightarrow NH_{ad}$ hydrogenation. The main purpose was to verify the role of extended defects and to specify the optimal catalytic centers in relevant reactions of $NO + H_2$ and $NH_3$ synthesis. Of course, the catalytic activity is contributed by a great number of independent and correlated parameters, and importance of each parameter depends on particular conditions. The present study focuses solely on defects without any intention of depreciating the role of perfect areas.

## 2. Theory

Thermodynamic properties of the adsorbed species were studied by semi-empirical Method of Interacting Bonds (MIB) which considers any polyatomic system as a set of two-center bonds [26–30]. Free atoms correspond to $H_0|\Psi_0\rangle = E_0|\Psi_0\rangle$ where $H_0$ and $\Psi_0$ are the Hamiltonian and the wave function of a ground state with energy $E_0$, respectively. A single *i*-th bond formation between adjacent atoms can be described with the perturbed potential $W_i^{'}$, wave function disturbance $\varphi_i$ and energy change $\varepsilon_i^{'}$ by $(H_0 + W_i^{'})|(\Psi_0 + \varphi_i)\rangle = (E_0 - \varepsilon_i^{'})|(\Psi_0 + \varphi_i)\rangle$. Since setting $\langle\varphi_i|\Psi_0\rangle = 0$ and $\langle\Psi_0|\Psi_0\rangle = 1$ do not affect generality, then $W_i^{'} = -\varepsilon_i^{'} + \frac{(E_0 - H_0)|\varphi_i\rangle}{\Psi_0 + \varphi_i} = -\varepsilon_i^{'} + W_i$. The arbitrary number of bonds conforms to $H = H_0 + \sum_i W_i^{'} = H_0 - \sum_i \varepsilon_i^{'} + \sum_i W_i$ with wave function of $\Psi = \Psi_0 + \sum_i \nu_i\varphi_i$ superposition. All $\varphi_i$, and therefore $W_i$, are assumed non-zero around *i*-th bond only, and a $\nu_i$ set corresponds to the minimal energy $E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$. Relevant calculation result in canonical relations for atomization enthalpy:

$$H_{at} = \sum_i \nu_i(2-\nu_i)E_i - \sum_{i>k}\sum \nu_i\nu_k\Delta_{ik}; \frac{dH_{at}}{d\nu_i} = 0 \tag{1}$$

where $E_i \equiv \frac{\langle\Psi_0|W_i|\Psi_0\rangle}{1+\sum_i\sum_k \nu_i\nu_k\langle\varphi_i|\varphi_k\rangle}$, $\Delta_{ik} \equiv \frac{2\langle\varphi_i|H_0 - E_0 + W_i + W_k|\varphi_k\rangle}{1+\sum_i\sum_k \nu_i\nu_k\langle\varphi_i|\varphi_k\rangle}$ and the most $\varepsilon_i^{'} << E_i$ [28].

The bond coefficients $\nu_i$ ($0 < \nu_i < 1$) follow from $i$ linear equations corresponding to the $H_{at}$ maxima. Empirical parameters $E_i$, $\Delta_{ik}$ are found from Eq. (1) and the reference $H_{at}$; $E_i$ and $\Delta_{ik}$ are set invariable for *i*-th bond and for the atom where *i*-th bond meets *k*-th one, respectively. The energy of the *i*-th bond breakage is ~$\nu_iE_i$; the exact energy accounts for removed repulsions and equals to difference between $H_{at}$ values of a system with and without *i*-th bond. The larger is the $\nu_i$ value, the stronger is the *i*-th bond, while negative $\nu_i$ means thermodynamic impossibility of bond formation; $E_i$ may be regarded as the bond energy of free two-atomic particle ($\nu_i = 1$).

MIB cannot predict molecular or crystal structures, atomic charges and other particular features, but it demonstrates perfect comparative accuracy and substantial time saving in comparison with conventional methods like Density Functional Theory (DFT). The equality of $E_i$, $\Delta_{ik}$ parameters of the reference and examined molecules (i.e. the same chemical bond nature) is the only condition for high reliability of MIB calculations within 0.5% [26]. MIB was applied to the following processes:

$$\tfrac{1}{2}\,H_2 \leftrightarrow \underline{H} + \tfrac{1}{2}\,Q_{H2}$$

$$\tfrac{1}{2}\,N_2 + \tfrac{1}{2}\,H_2 + M_n \rightarrow \underline{NH}\,(M_n) + Q_{NH} \tag{2}$$

$$\tfrac{1}{2}N_2 + M_n \leftrightarrow \underline{N}(M_n) + Q_N \tag{3}$$

$$\underline{N} + \underline{H} \rightarrow \underline{NH} + Q_{\underline{NH}}. \tag{4}$$

Hereinafter the adsorbed states are underlined in italic; $M_n$ is the adsorption/catalytic site consisting of $n$ adjacent atoms, each bound to the adsorbed species; H atom in $\underline{NH}$ particle is bound to N and not to M atom; $H_2$ adsorption is assumed to be equilibrium process; both equilibrium and dynamic conditions for $\underline{N}$ and $\underline{NH}$ species are considered.

Atomization enthalpy of $\underline{N}$ and $\underline{NH}$ species at the given $M_n$ site is a direct result of calculation. Free atoms at standard conditions (298.15 K;

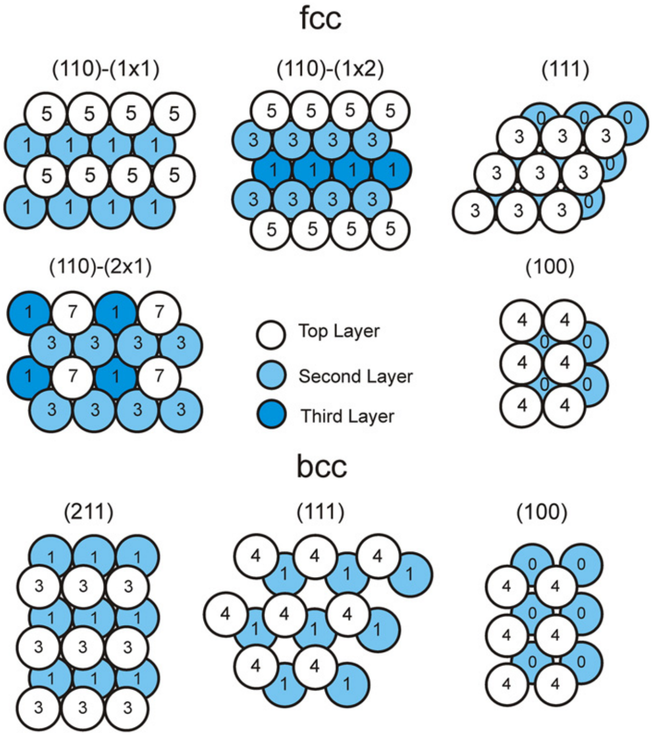

**Fig. 1.** Individual numbers of bonds $\eta$ lost by atoms on indicated planes.

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