



Adjustment of active sites in catalytic ammonia synthesis over metal alloys and clusters: A theoretical study

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ABSTRACT

Earlier, a theoretical model was suggested to discriminate catalytic sites M_n (each consisting of n adjacent atoms M on the metal surface) according to their undercoordination Σ . It has been shown that the maximum activity of a site M_n ($M = \text{Pt, Rh, Ir, Fe, Ru, Re}; n = 2, 3, 4$) in the catalytic synthesis of ammonia requires the “resonant” Σ , whose major part is inaccessible at perfect planes because of steric restrictions. The current study applies this model to binary alloys and clusters to construct an advanced catalytic site by adjustment of real Σ to the resonance. The catalytic activity of a site M_n has been estimated by the Brønsted-Evans-Polanyi relation with respect to the formation of NH species. It was found that on alloy surfaces, sites M_3 and M_4 demonstrate synergetic behavior. This suggests that the most active catalyst (Ru or Re) can be improved by its alloying with the least active one (Pt or Rh). In the case of the noble metals, the sites M_3 and M_4 at 4-, 5-, and 11- atomic clusters are $\sim 10\text{--}10^3$ times more active than such sites at perfect planes, whereas the sites of Ru and Re show the opposite behaviour. The model was verified by comparison of the calculated specific catalytic activities of metals, centers Fe-C₇ and Ru-B₅, and single crystals with the published data. The superior activity of a catalytic site is generally enabled by its optimal thermodynamics, which is affected deeply by the first coordination shell. A correlation between local structure, thermodynamics, and activity of a site is likely valid for other catalytic systems.

1. Introduction

The surface of a catalyst usually exhibits its activity at small atomic ensembles of a particular structure and composition, known as active sites [1–3]. Reliable knowledge on these sites forms the grounds for the development of advanced catalysts and helps to elucidate the reaction mechanism. Surface defects are also often regarded as active sites for target reactions despite their activity in inhibitor accumulation and trapping of charged species [4,5]. Some point and extended defects can be active sites for adsorption, surface reactions, or cluster nucleation [6]. For example, structural imperfections can catalyze the reduction of NO by H₂ on several metal surfaces [7–9] and the reaction CO + O₂ on Pt single crystals [10]. The well known dependence of the catalytic activity on the particle size emphasizes the role of such local structures as well [1,11,12]. Availability of the structural defects may be a necessary condition for a catalytic process, and the existence of structure-sensitive reactions confirms this speculation [13–16]. Needless to say, the amount of evidence on the structure-activity interrelation of the catalytic sites grows continuously [17,18].

A substantial number of basic concepts of heterogeneous catalysis have been discovered during the development of the Haber–Bosch process, which can be regarded as a benchmark in the field [19,20]. Various studies of this process have shown that the catalytic ammonia synthesis is a structure-sensitive reaction [11,21–24]. For example, the

superior activities of Fe(111) and (211) single crystals in this reaction were attributed to the formation of a C₇ center, corresponding to a 7-coordinated Fe atom in the second surface layer [12,25]. It was also shown that similar centers on the Ru surface exhibited no specific catalytic activity, while the enhanced activity of certain crystal faces of Ru was related to their large roughness and openness [11]. Later, the high activity of Ru-based catalysts was attributed to the formation of some B₅ centers [21,26,27]. In the subsequent papers, catalytic activities of metal surfaces in the ammonia synthesis were correlated with heats of the bulk oxide formation, initial heats of the N₂ adsorption, a chemical nature of promoters and supports, a size distribution for the supported substrate, etc. Nevertheless, the exact nature of the active sites, as well as the mechanism of their catalytic promotion, remains a matter of discussion [2,28–33].

The concept of active sites is fundamental for heterogeneous catalysis; however, it has not much changed since the time of Taylor [34]. The superior chemical activity of a radical or a free atom is generally attributed to its valence unsaturation. All heterogeneous catalytic processes follow basic chemical concepts, and it seems reasonable to regard an undercoordination of near-surface atoms as, in no small measure, being responsible for the catalytic activity [28,35]. The scission of a solid into two parts increases the enthalpy of a system by two surface energies, and this reserve can indeed compensate, completely or partially, the activation energy for a chemical reaction in the adsorbed

layer. For instance, a catalytic combustion is an example of the complete compensation [36], while a partial compensation can enable some mild catalytic promotion. We evaluated the undercoordination Σ of a site M_n in common terms and approximated its activity in the catalytic ammonia synthesis using equilibrium coverage of NH species [37]. This approach has revealed strong dependence of the catalytic activity of sites on their Σ . The highest activity of a site M_n eventually required the “resonant” Σ value, whose major part is not accessible at perfect planes because of steric causes. The present study considers sites M_n ($n = 2; 3; 4$) on several surfaces of binary Pt-, Rh-, Ir-, Fe-, Ru-, and Re-based alloys and small clusters to fit the real Σ to the resonance. The objects, such as basic planes, nanoparticles, and alloys, have shown a good reputation for the fundamental and applied studies regardless the process considered [28,38]. Therefore, the results of this work can be useful for other catalytic systems as follows. First, one has to determine such a resonant undercoordination of a catalytic site (or a set of sites) that provides its maximum activity in the rate-determining step (RDS) of a particular reaction. Then, one should choose such experimental conditions (an open or close-packed structure of the catalyst surface, a size of supported particles, or a composition of the complex substrate) that can provide the best possible agreement of accessible Σ values with the relevant resonance.

2. Theoretical

2.1. Model

In terms of general chemistry, each atom on the surface of a solid can be characterized by its undercoordination, i.e. by the number of deficient nearest neighbors as compared with the bulk atom. For example, the atom in the bulk of the face-centered cubic (fcc) lattice lacks 0 of 12 nearest neighbors, whereas the atom at the perfect fcc plane lacks from 1 to 7 nearest neighbors (Fig. 1 and Supplementary data, Fig. S1). Let accept a set of n adjacent near-surface atoms M , each bound to the adsorbed species, as an adsorptive or catalytic site M_n . The Σ model considers a sum of under coordinations of the atoms in a site M_n as a structural descriptor Σ , which can be also regarded as a degree of the local imperfection or valence unsaturation. In addition, the heat Q_i of adsorption or chemical transformation of the adsorbed species on a site ΣM_n is used for the evaluation of its activity. At that, it does not matter whether the adsorption or reaction is equilibrium or not, according to the Brønsted-Evans-Polanyi (BEP) relationship, which states that the higher is the heat of the process, the lower is the activation barrier, and thus the more active it is [37]. A similar correlation is widely used elsewhere [39–42].

Table 1

Empirical parameters, half heats of H_2 adsorption Q_H [37], and standard enthalpies of atomization $\Delta_f H^\circ$ (kJ/mol) [44].

	E_{MM}	Δ_M	E_{MN}	Q_H	$\Delta_f H^\circ$	E_{NH}	Δ_N
Pt	334.3	77.7	384.9	33.5	565.3	596.4	313.8
Rh	333.0	77.4	405.8	38.9	556.9		
Ir	392.9	91.4	453.1	41.6	665.3		
Ru	381.1	88.6	520.4	43.5	642.7		
Re	456.6	106.2	555.3	41.7	769.9		
Fe bcc	273.5	63.6	404.5	41.5	416.3		
Fe fcc	246.3	57.3	404.5	41.5			

2.2. Method

A method for the accumulation of the dataset $\{Q_i\}$ for numerous sites ΣM_n should be sensitive to the coordination number and must provide a suitable speed/accuracy ratio. In this context, the preference in our study was given to the semi-empirical Method of Interacting Bonds (MIB) [37,43, and Supplementary data], which considers the polyatomic system as a set of two-center bonds and gives the following basic relations for the enthalpy of atomization:

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

$$\frac{dH_{at}}{d\nu_i} = 0 \quad (1)$$

Here, empirical parameters E_i and Δ_{ik} account for the strength of an i -th bond and for the repulsion between the i -th and a k -th bond of the same atom, respectively; the bond coefficients n_i ($0 < n_i < 1$) are found from i linear equations corresponding to H_{at} maxima.

The parameters E and Δ are the property of a particular bond and of an atom, respectively. For example, one just needs to know E_{MM} and Δ_M to calculate the formation enthalpy of any chemical combination of atoms M . The empirical parameters in Table 1 were determined by Eq. (1) using reference enthalpies of the formation of bulk phases and the free molecule of NH_3 . The empirical correlation $E_{MM}/\Delta_M = 4.3$ was used for all substrates [37,45]. The same nature of a bond in reference and examined molecules (i.e. an equality of relevant E and Δ values) is the only condition for reliability and high comparative accuracy of the calculations (Supplementary data, Table S1). In contrast to the Density Functional Theory (DFT), the MIB uses coordination number as an operational parameter. In addition, for a similar thermodynamic output, the overall MIB processing requires much shorter time as compared with a DFT run [45].

In our calculations, a unit cell representing the semi-infinite single crystal included 18–20 atoms. It required varying 57–66 parameters ν_i

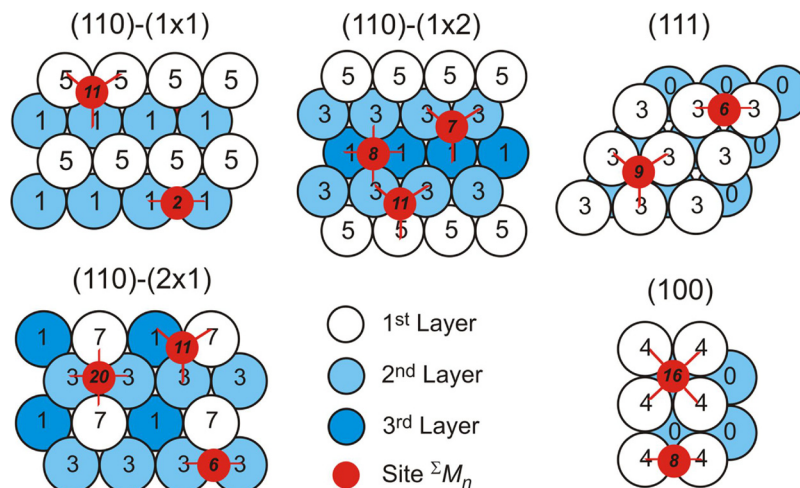


Fig. 1. Sites ΣM_n ($n = 2, 3, 4$) on basic planes with the fcc structure; undercoordination of the atoms and Σ of sites are indicated.

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