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NO dissociation and reduction by H_2 on Pd(1 1 1): A first-principles study

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ABSTRACT

Periodic density functional theory (DFT) calculations were carried out to elucidate the reaction mechanisms of NO reduction by H_2 and possible products on Pd(1 1 1). The results show that direct NO dissociation is unlikely due to high-energy barrier; alternatively, NO dimer exists on Pd(1 1 1) surface followed by the N–O bond scission to form N_2O. The presence of H_2 promotes the NO dissociation. The N_2 formation pathway is $NO + N \rightarrow N_2 + O$ rather than $N + N \rightarrow N_2$. Besides, N_2 is formed preferentially than N_2O from the coadsorbed state of NO + N. The NH_3 formation comes from the successive hydrogenation reactions of nitrogen and the NH formation is the rate-determining step. The microkinetic analysis further confirms that N_2O is major at low temperature while N_2 becomes dominant as temperature increases. The selectivities toward N_2 and NH_3 shift to slightly lower temperature as H_2/NO ratio increases.

1. Introduction

NO is an important pollutant produced from industrial and automotive exhausts. The emission of NO not only causes a series of environmental problems such as photochemical smog, acid rain and ozone depletion [1–3], but also has adverse effect on humans. Therefore, the catalytic removal of NO has become one of the most important problems for air pollution control and attracted remarkable attention in both academic and applied research fields [4]. In the automotive industry, platinum group metals (PGMs) such as Pt, Pd, and Rh as the main components are involved in the three-way catalysts, which have often been used for the catalytic reduction of NO for several decades [5,6]. However, the O atom produced from NO dissociation usually has strong adsorption energy on PGMs, which poisons the catalysts and thereby limiting the low-temperature activity of PGMs for NO decomposition. Currently, selective catalytic reduction (SCR) has been widely considered as one of effective approaches for the removal of NO employing ammonia, carbon monoxide, hydrogen as well as hydrocarbons (HC_s) [7–11] as reducing agents and has been introduced in many material applications. Among these reducing agents, hydrogen, which is produced in the automotive and stationary sources (from water–gas-shift reaction or from hydrocarbons), was reported to be very effective in the catalytic reduction of NO_x (H_2-SCR) to N_2 especially under lean-burn conditions. Also, the combustion of H_2 producing water makes H_2-SCR to be a green environmental technology. Therefore, the SCR of NO by H_2 over the noble metal-based catalysts has attracted much attention experimentally and theoretically [3,12–22].

There are extensive experimental studies for the selective reduction of NO with H_2 on Pd-based catalysts since Pd is cheaper, highly abundant and has good thermal stability. For example, on the clean Pd(1 1 1) surface [22], de Wolf et al. studied the NO–H_2 reaction at different H_2/NO ratios and demonstrated that H_2 promotes the NO dissociation and the excess H_2 contributes to the mass production of byproduct NH_3. Ma et al. [16] studied the surface nitrogen removal pathways of NO + H_2 reaction on Pd(1 1 0) and concluded that the reduction of NO by H_2 shows not only a higher reactivity but also a higher selectivity toward N_2 compared with the reduction by CO. Among the studies of NO + H_2 reaction on different Pd-based catalysts, the Pd/TiO_2 catalyst was proved to possess higher NO_x conversion than Pd/Al_2O_3 [21], and the ZrO_2-supported Pd nanocatalysts were reported to present both high reactivity for NO and high selectivity toward N_2 [3]. In addition, for the different metal-based catalysts for NO reduction by H_2, Roy et al. [19] studied four various TiO_2-supported metallic catalysts such as Ru, Rh, Pt, and Pd, and found that Pd/TiO_2 catalyst possess both the low-temperature catalytic activity and selectivity. These results show that Pd metal catalysts are very effective for the selective reduction of NO by H_2. Contrary to the extensive experimental reports, few theoretical studies have been carried out to understand the NO + H_2 reaction on Pd-based catalysts. To provide a deep insight into the intrinsic property of Pd catalyst, the elucidation of selective catalytic reduction process of Pd without support material is very desirable. Since the close-packed (1 1 1)

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facet was found to be the dominant facet in real supported palladium catalysts, in this work, we choose the Pd(111) surface as our DFT model system [23–25]. Knowledge of the reaction process for NO reduction by H_2 on Pd(111) surface at the fundamental level is very limited. For example, what is the rate-limiting step for NO conversion to N_2? How does H_2 influence the products formation and selectivities of the possible products such as N_2, byproducts N_2O, and NH_3 during the catalytic process? What is the main pathway for N_2 formation? In addition, interestingly, $(NO)_2$ dimer was observed at room temperature by using infrared spectroscopy on Pd(111) surface recently, as demonstrated in the literature on some other surfaces including Au [4], Ag [26], Cu [27–29], Mo [30], Rh [31], Al_2O_3 [32], MgO [33], and Si-doped graphene [34]. In experiment, N_2O was observed at low temperature on ZrO_2-supported Pd nanocatalysts [3]. So what is the mechanism for the N_2O formation on Pd(111), via the direct mechanism ($NO \rightarrow N + O$, $N + NO \rightarrow N_2O$) or a dimeric mechanism ($2NO \rightarrow (NO)_2 \rightarrow N_2O + O$) same as that on the Au(111) [4] and Ag(111) [26] surfaces? To address the above issues, in this paper, we investigated the selective reduction of NO with H_2 on Pd(111) surface by means of the first-principles density functional theory calculations. Furthermore, a simple microkinetic model was developed to predict the reactivity and product selectivity of Pd catalyst. The rate constant of each elementary step was calculated by the harmonic transition state theory on the basis of the DFT results [35,36]. The modeling results were compared with experimental reaction kinetic data.

2. Computational details

All periodic DFT calculations were carried out using the Vienna ab initio simulation package (VASP) [37,38]. The generalized gradient approximation (GGA) with the function of Perdew and Wang (PW91) [39] was considered to deal with the exchange–correlation energies, and the electron–ion interactions were described by the projected augmented wave (PAW) method [40,41]. A plane-wave basis set with an energy cutoff of 400 eV was used to expand the one-electron wave function. Brillouin zones were sampled with a grid of 7 × 7 × 1 Monkhorst–Pack [42] special k-point for surface calculations and spin polarization was considered in all calculations.

The optimized lattice constant of bulk Pd is 3.95 Å, in good agreement with the experimental result of 3.89 Å [43]. In the present study, the Pd(111) surface was modeled using a five-layer slab with a 2 × 2 unit cell corresponding to 0.25 ML at the experimentally determined lattice constant. A vacuum region of eight-layer thickness was used to remove any interactions between slabs. The three upper Pd atom layers were allowed to fully relax while the two lower layers were fixed. The geometry optimization was stopped when the forces on all unconstrained atoms were less than 0.02 eV/Å.

The climbing-image nudge elastic band (CI-NEB) method [44,45] was employed to determine the transition states (TSs) and the minimum energy pathways (MEPs) were constructed accordingly. The harmonic vibrational frequency calculations were performed to ensure that the minima possess all real frequencies and transition states have one imaginary frequency. In this procedure, all the metal layers were fixed and the adsorbates were allowed to relax. The adsorption energies (E_{ads}) of all the possible adsorbates were defined by the following standard equation:

$$E_{ads} = E_{gas\text{-}surf} - (E_{surf} + E_{gas})$$

where $E_{gas\text{-}surf}$, E_{surf}, and E_{gas} are the total energies of the adsorbed system, the clean surface and the corresponding gas phase species, respectively. Zero-point energy (ZPE) corrections were included in all the energy calculations. The interaction energy was also considered which was defined as the difference between the energies of the coadsorbed configuration and infinite separation state (each adsorbate in a separate unit cell at its most stable position). The energy barriers of the bimolecular reactions were calculated based on the energy difference between the transition state structures and the reactants in infinite separation state.

3. Results and discussion

There are four typical adsorption sites on the Pd(111) surface, i.e., top (T), bridge (B), hcp (H), and fcc (F) sites. The preferential adsorption of all surface species involved in the $NO + H_2$ reaction and the corresponding adsorption energies are compiled in Table 1. The likely reaction pathways of NO dissociation and the formation of possible products were considered, but only the minimum energy paths of each elementary step were reported. In the diagrams, $A^{*}\cdots B^{*}$ denotes the co-adsorbed state of species A and B, and $A^{*} + B^{*}$ denotes the infinite separations with each adsorbate (A^{*} or B^{*}) in separate unit cell at its most stable position. Finally, based on the DFT calculated results, we established a simple microkinetic model to discuss the possible product selectivity.

3.1. Adsorption of surface species on Pd(111)

3.1.1. Adsorption of N_mO_n fragments ($m, n = 0–2$)

NO prefers to bind uprightly through the N atom at two threefold hollow sites, with similar adsorption energies of −2.16 eV at fcc site and −2.12 eV at hcp site, as shown in Fig. 1. The N–O bond lengths are 1.206 and 1.205 Å, respectively, slightly larger than that 1.17 Å in gas phase. Our calculated adsorption energy at fcc site is slightly larger than the value of −2.07 eV [46] and less than the value of −2.34 eV obtained by the PBE functional [47].

Two stable $(NO)_2$ dimeric isomers (*cis*-$(NO)_2$ and *trans*-$(NO)_2$) were located on Pd(111), in which two NO molecules link to each other through N atoms, similar to the dimer structures which were also found on the Au(111) surface, but on Ag(111) only *cis*-$(NO)_2$ was located. On Pd(111) surface, the *cis*-$(NO)_2$ isomer is adsorbed at the fcc site in the η^1(O)–N–N–η^2(O) mode, i.e., one O atom binds at a top site, while the other O binds at the opposite bridge site, with the adsorption energy of −1.48 eV with respect to two NO molecules in the gas phase. The N–N distance is 1.23 Å, which is much shorter than that of the free *cis*-$(NO)_2$ in gas phase (1.986 Å), while very close to the distance (1.26 Å) of the $(NO)_2$ dimer on Ag(111) [26] and slightly less than that (1.47 Å) on Au(111) [4] surface. The *trans*-$(NO)_2$ isomer can adsorb at both fcc and hcp site in the O–η^1(N)–N–η^2(O) mode. Same N–N distance (1.33 Å) is obtained in the two configurations, which is very close to the value (1.30 Å) on the Au(111) [4] surface, while is much shortened from that (1.943 Å) in the gas phase. The calculated adsorption energies for the two sites are −1.76 and −1.74 eV relative to two free NO molecules, respectively. Thus, the *trans*-$(NO)_2$ is energetically more stable than *cis*-$(NO)_2$ on Pd(111) by about 0.28 eV.

N_2O weakly binds at the top site through its terminal N to the Pd atom with a small adsorption energy of −0.14 eV, which agrees well with the previous DFT result of −0.12 eV obtained by Wei et al. [48]. The whole molecule keeps straight line and has an angle of 34° from the surface normal with the N–N and N–O distances of 1.15 and 1.20 Å, respectively.

N_2 adsorbs perpendicularly at the top site with the N–Pd and N–N bond lengths of 2.03 and 1.12 Å, respectively. The adsorption energy is −0.17 eV, which is slightly less than the previous calculated value of −0.23 eV [46]. The parallel adsorption of N_2 at the bridge site in the η^1(N)–η^1(N) (di-σ) mode is less favorable with