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Structure and catalytic processes of N-containing species on Rh(111) from first principles

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Abstract

Density functional theory has been used to gain molecular understanding of various catalytic processes involving N species on Rh(111). These include CN, N_2, and HCN formation and N_2O decomposition. Our calculations substantiate the conclusion that, starting from chemisorbed C and N atomic species, CN formation is preferred over N_2 formation, because of the lower activation energy of the former process (1.73 vs. 2.10 eV). HCN formation has been studied starting from adsorbed CH and N species, with a computed activation barrier of 1.35 eV. The process of binding CH to N is more favorable than recombination of C and N atoms into CN followed by hydrogenation. Concerning the adsorption and dissociation of N_2O on Rh, two pathways have been investigated, leading to N_2 or NO. From thermodynamic considerations, N_2 can be concluded to be the preferred product resulting from N_2O dissociation. Our results also support the participation of N_2O as a reaction intermediate during reduction of nitric oxide to nitrogen over Rh surfaces by reaction of adsorbed NO and N atoms.

Keywords: First principles; DFT; Chemisorption; Catalysis; Rhodium; Rh(111); N species; CN; HCN; N_2O

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1. Introduction

Heterogeneous catalysis is the basis for the majority of chemical production processes in industry. In the last 10 to 20 years, significant advances have been made in acquiring a deeper mechanistic understanding of catalytic processes by the application of novel surface science techniques with model surfaces under ultrahigh-vacuum conditions [1–3] and theoretical approaches based on quantum chemical principles [4–8]. Ab initio theoretical methods have now reached the point where molecular structures and adsorbed species on solid surfaces are predicted with accuracy comparable to that of the most sophisticated experimental methodologies. This provides information about the nature of the active sites, adsorbate structure, adsorption and activation energies, and reaction paths, which is essential information for reactor design and process scale-up. Computational approaches can be of significant help in the rational catalyst design of new and well-established processes. This is excellently exemplified by recent work from Jacobsen et al. [9], who accomplished the computational development of novel Co–Mo alloys for ammonia synthesis displaying higher activities than the typical Fe- and Ru-based catalysts.

In this paper we apply density functional theory (DFT) calculations to periodic models to gain a mechanistic insight into various catalytic processes involving N-containing species on rhodium surfaces. Cases subjected to study include the structure and formation of CN, N_2, and HCN adsorbed species and the adsorption and dissociation reactivity of N_2O on Rh(111) and its involvement as a reaction in-

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termediate in de-NO_x reactions. The mechanisms of these particular processes have not been fully resolved yet, particularly with regard to the aspects mentioned below.

1.1. CN and HCN formation

HCN is typically found as an unwanted product in the reduction of nitric oxide (NO) by hydrocarbons on rhodium catalysts in car exhaust purification [10]. This process likely involves the presence of surface cyanide (CN) species as a reaction intermediate. CN can be formed by the recombination of adsorbed C and N atoms [10–14]. Van Hardeveld et al. studied the reaction of NO [10] or atomic nitrogen atoms [11] with ethylene (C_2H_4) on Rh(111). The main product of the reaction at low ethylene doses was N_2. However, the selectivity of the reaction for HCN increased with increasing ethylene exposure, thus suggesting that cyanide formation occurs via the reaction between adsorbed N atoms with atomic adsorbed C atoms or hydrocarbon fragments. Moreover, it was reported that whereas N_2 desorbs normally between 500 and 750 K from Rh(111), desorption was retarded at higher temperatures (650–850 K) after exposure to ethylene. This was attributed to CN formation, and, in the absence of surface hydrogen, these CN groups were found to be stable up to $\sim$ 700 K. Herceg and Trenary [12], investigating the $CH_3I + NH_3$ reaction on Pt(111), also concluded that the C–N coupling occurs via interaction of adsorbed C and N atoms.

1.2. Processes involving N_2O

Nitrous oxide (N_2O) is a harmful gas in our environment, contributing to ozone layer depletion and the greenhouse effect. The major industrial source of N_2O is the production of nitric acid. Other sources are production plants that produce adipic acid, caprolactam, glyoxal, and acrylonitrile, and, in general, processes using HNO_3 as the oxidant or involving oxidation of ammonia [15,16]. Direct catalytic decomposition of N_2O into N_2 and O_2 represents an attractive and cost-effective technology for reducing emissions in tail gases [16]. Rh-based catalysts on different supports, including single and mixed oxides and zeolites, have been considered the most active systems for direct N_2O decomposition at low temperatures. Although there are some theoretical studies that deal with N_2O adsorption to metal surfaces, including Pd, Cu, Ni, Pt, and Rh [17–23], the mechanisms for N_2O formation and dissociation are not yet fully understood.

In addition, the occurrence of N_2O as a possible reaction intermediate in the mechanism of NO reduction to N_2 over Rh-based catalysts is controversial and remains unsolved [24]. An accepted description is that after NO dissociation the resulting N surface atoms recombine, yielding N_2 [25]. Whereas Belton el al. [26] discarded the involvement of N_2O in the NO + N reaction over Rh(111), Zaera and Gopinath [27,28] postulated that N_2O is an intermediate during the reduction of NO with CO to N_2 over Rh(111). Ma et al. [29] indicate that N_2 is produced via N_2O as an intermediate species at $T \leqslant\sim 600$ K in the NO + CO reaction on Pd(110), although at higher temperatures the associative desorption of nitrogen atoms prevailed. It has also been shown that molecular oxygen is produced via both interaction of N_2O with adsorbed oxygen species formed from N_2O and recombination of adsorbed oxygen species on the surface over a Pt–Rh alloy gauze catalyst [30]. On this basis competitive decomposition of adsorbed N_2O into N_2 or NO can be envisaged, although the formation of NO upon interaction of N_2O with catalytic surfaces in steady-state or transient experiments, where N_2 and O_2 are the decomposition products, has not been reported in the literature.

2. Computational details

The Rh(111) surface was modeled by a three-metal layer periodic slab with seven vacuum layers and a $p(3 \times 3)$ unit cell for the study of CN and HCN. To study the reactivity of N_2O we considered five metal layers and a $p(2 \times 2)$ unit cell. The positions of the Rh atoms were taken from the optimized value for the bulk lattice parameter of 3.849 Å, which is very close to the experimentally determined value of 3.803 Å. In the case of CN and HCN, the rhodium atoms of the first surface layer were allowed to relax, while the other two layers were frozen. In the case of N_2O the three upper layers were relaxed, although the relaxation of the second layer was smaller than $\sim 0.2\%$

The calculations were performed in the framework of density functional theory, with the use of periodic models and the Vienna Ab Initio Simulation Package (VASP) [31–33]. The exchange-correlation functional used was the gradient-corrected form proposed by Perdew and Wang (PW91) [34]. The electron–ion interaction is described by ultrasoft pseudopotentials [35] with a cutoff energy for the plane-wave expansion of 400 eV. Brillouin-zone integration was performed with grids of $6 \times 6 \times 1$ Monkhorst-Pack [36] special k points. The optimization of the atomic positions is performed via a conjugate gradient minimization of the total energy using the Hellmann–Feyman forces on the atoms. We used the climbing-image nudged-elastic-band method (CI-NEB) [37] to obtain minimum energy pathways and transition-state structures.

The adsorption energies (E_{ads}) were calculated according to $E_{\mathrm{ads}} = E_{\mathrm{mol/sub}} - (E_{\mathrm{mol}} + E_{\mathrm{sub}})$, where E_{sub} is the empty substrate energy, E_{mol} is the energy of the molecule in the gas phase, and $E_{\mathrm{mol/sub}}$ is the energy of the adsorbed molecule. A negative value of E_{ads} indicates an exothermic process. Since the CN radical is not stable in the gas phase, the adsorption energy is referenced to $\frac{1}{2}$ C_2N_2.