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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

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 $E_{ads} = E_{mol/sub} - (E_{mol} + E_{sub})$, where E_{sub} is the empty substrate energy, E_{mol} is the energy of the molecule in the gas phase, and $E_{mol/sub}$ 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 $\frac{1}{2}\ C_2N_2$.

3. Results and discussion

3.1. CN and HCN production

3.1.1. CN, HCN, and N_2 adsorption modes

First we investigated the adsorption of carbon and nitrogen atoms on the Rh(111) surface. Carbon and nitrogen have a similar energy profile; the preferred adsorption site is the hcp threefold hollow site, with an adsorption energy of −8.12 eV for atomic carbon and −5.40 eV for atomic nitrogen, with respect to the atoms in the gas phase. Subsequently, the binding of CN species to the surface was explored. The most stable CN adsorption mode molecule is perpendicular to the fcc site with an adsorption energy of −4.02 eV with respect to the CN radical in the gas phase, which corresponds to −0.85 eV with respect to $\frac{1}{2}$ C_2N_2. The C–N distance is 1.20 Å, only slightly larger than the value for the gas-phase CN radical (1.17 Å). However, as shown in Fig. 1, other modes (on top, bridge, hcp, or even bidentate structures are within a narrow range of energy between −0.61 and −0.85 eV, with respect to gas-phase cyanogen). This adsorption mode is different on surfaces such as Pt(111) [38,39], where the most stable configuration is the top site, with an adsorption energy of −3.64 eV with respect to CN or −0.47 eV with respect to $\frac{1}{2}$ C_2N_2. As in the present study, several adsorption modes appeared to be feasible in a narrow range of adsorption energies on Pt(111). Similar results were also reported for CN on Ni [40] or Au [41] surfaces. The adsorption of molecular nitrogen on the surface is stable only on top sites with an adsorption energy of −0.50 eV, with the N–N bond perpendicular to the metal surface.

Fig. 2 shows the structures and energetic levels for the more stable stationary points of HCN adsorbed to Rh(111). The most stable adsorption mode is on the hcp site via the C atom. The adsorption energy with respect to HCN in the gas

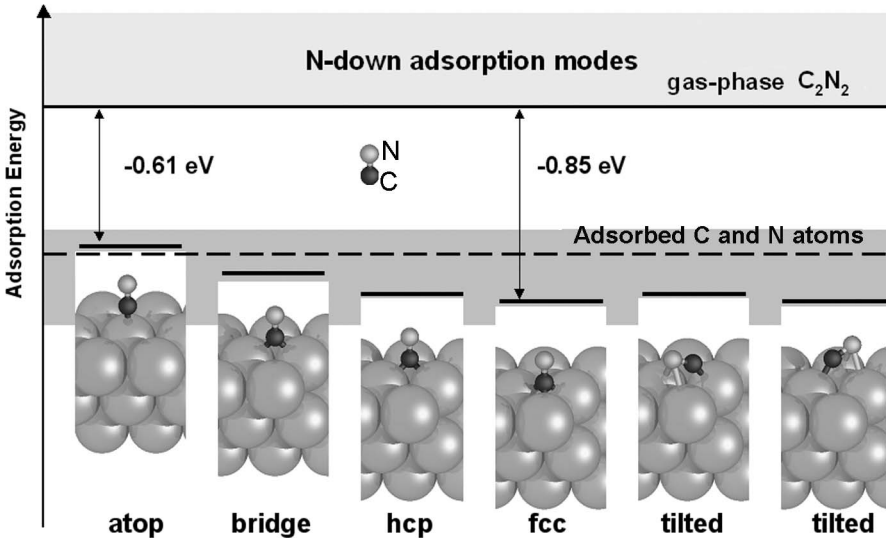

Fig. 1. Adsorption of CN on Rh(111). Only the modes with the C-atom bound to the surface are shown: top, bridge, hcp, fcc, and two tilted modes. The adsorption energy of the co-adsorbed C + N atoms is represented by the thick dash-line.

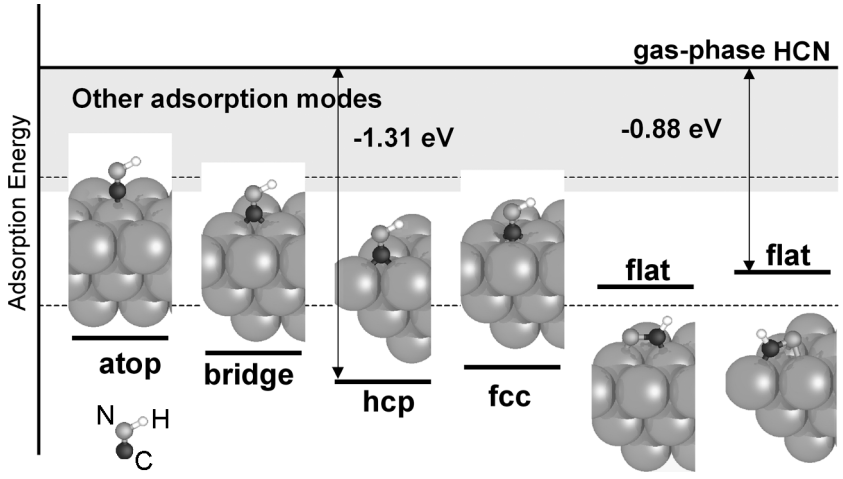

Fig. 2. Adsorption of HCN on Rh(111); only the modes in which HCN binds through the carbon atom and two tilted modes are shown.

phase is −1.31 eV. The C–N distance is 1.24 Å in the adsorbate, longer than for the gas-phase molecule (1.17 Å), with an H–C–N angle of 124°. We have also explored the different structures (not shown in Fig. 2) bound to the surface via N; these are always less stable than those bound through the C atom of HCN. Finally, we located two η_2 flat modes with the H atom linked to C or N, which are nearly degenerate in energy.

3.1.2. Selectivity for CN and N_2

Fig. 3 shows a pathway for the formation of a CN species bound through C from the atoms, in which the N atom moves toward the C atom. The calculated activation energy for cyanide formation, from its constituent atoms adsorbed at threefold hcp hollow sites, is 1.73 eV, whereas the CN decomposition has a somewhat higher activation energy of 1.89 eV. Accordingly, the exothermicity amounts to only −0.16 eV. The structure of the transition state, where C is at the hollow site and N is near the bridge site, agrees with the results from Michaelides and Hu for the same reaction on Pt(111) [42], although the barrier on Pt(111) was significantly lower (0.82 eV). This provides additional support to the hypothesis of Michaelides and Hu that in this type of reaction on metallic (111) surfaces, the adsorbate with a lower valence is activated over the bridge site. An alternative minimum-energy pathway where the C atom moves to N to form adsorbed CN also via C has been calculated as well. The energy barrier for this path is 1.79 eV, a value only slightly higher than the previous one.

The formation of N_2 follows similar trends, but, in this case, the transition state is formed by two N atoms in hollow sites. The path leads to N_2 adsorbed to a hollow site, which subsequently may shift to the top position, with an additional energy gain of −0.6 eV. Alternatively, N_2 may desorb. The exothermicity for the recombination of adsorbed nitrogen atoms is −0.35 eV, slightly higher than for CN formation, but the calculated activation energy is 2.10 eV, which is larger than that for CN formation. This explains the preferential formation of adsorbed CN over N_2 as observed in a temperature-programmed experiment [11]. Moreover, the stability of the CN species on Rh(111) is closely related to the fact that there are several adsorption modes for CN within a narrow range of adsorption energies. Hence, the CN species is likely to have a high mobility on the surface, and therefore dissociation of CN through an immobilized or tight transition state [5] would mean a considerable loss of entropy. As this is by no means compensated for energetically, dissociation of CN is unfavorable and therefore possible only at elevated temperatures, as indeed observed by Van Hardeveld et al. [10,11].

3.1.3. Formation of HCN

A minimum-energy pathway for HCN formation has been obtained, starting from adsorbed CH and N species and concluding with a flat adsorbed HCN (Fig. 4). The most favorable position for the CH species is the hcp hollow site, with a formation energy of −0.45 eV with respect to adsorbed H and C atoms. In the pathway, the N atom moves toward the CH species. The energy barriers for the formation of HCN and decomposition are 1.35 and 1.05 eV, respectively. The transition state is above the energy for the free molecule. If we start from C, N, and H adsorbed to Rh(111) and disregard the presence of NH on the surface [11], two possibilities can be conceived for HCN formation: (a) CH formation and reaction with N or (b) CN formation and hydrogenation [11]. As we have seen, the barrier for the HCN formation from CH and N (1.35 eV) is smaller than that for CN formation (1.73 eV). On the other hand, the energetic barrier for CH formation is predicted to be on the order of ∼ 0.5 eV [43], much lower than that for CN formation. Thus, the path that binds adsorbed CH and N is energetically favored over formation of CN and its hydrogenation. This supports TPD results reported by Herceg and Trenary [12]. They found that the C–N coupling cannot occur directly by reaction of CH_3 and NH_3 and, accordingly, must proceed through their dissociation products. However, the same authors also observed that in the absence of CH_x and NH_y species the C–N coupling takes place directly from adsorbed C and N atoms. Adsorbed CH is predominant in the decomposition of hydrocarbons like ethylene [1]. There-

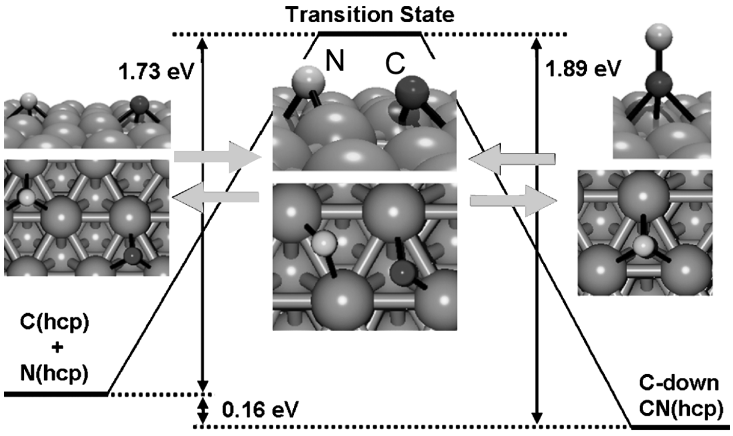

Fig. 3. Reaction and transition state geometry for CN formation from adsorbed C and N atoms on Rh(111).

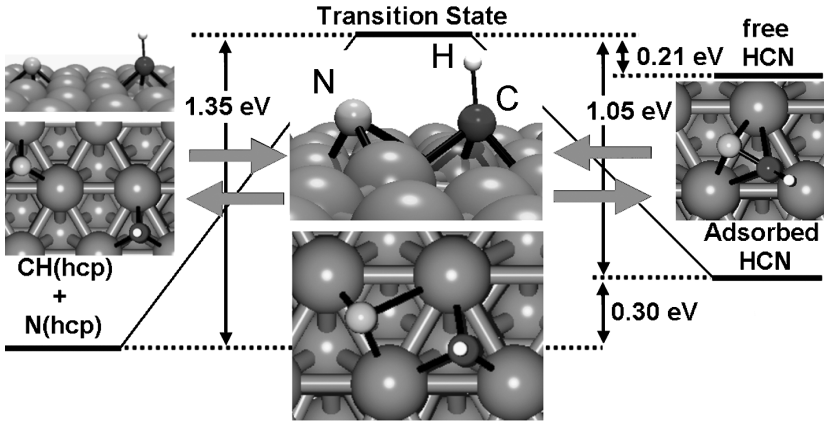

Fig. 4. Reaction and transition state geometry for HCN formation from adsorbed CH + N on Rh(111).

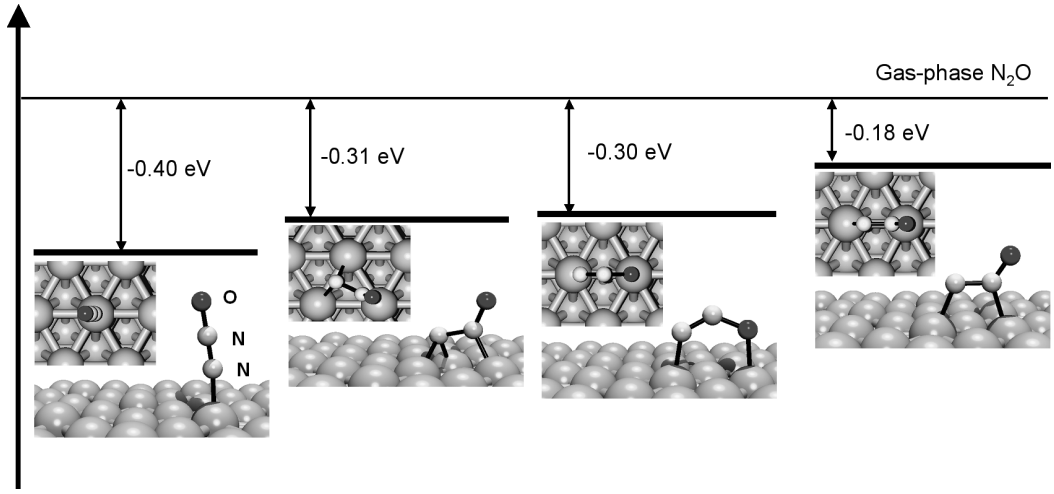

Fig. 5. Structures of the most stable modes of adsorbed N_2O on Rh(111).

fore, the formation of HCN via the CH fragments is plausible and energetically favored and in agreement with experimental findings.

3.2. N_2O decomposition

3.2.1. N_2O adsorption

We explored the various adsorption modes of N_2O, including two η_1 modes (by N_t or O) and three η_2 modes (N_t,N_c, N_t,O, and N_c,O, where t stands for terminal and c for central). The most stable system corresponds to adsorption through the terminal N_t atom on top of one Rh atom, with an adsorption energy of -0.40 eV (Fig. 5). The molecule is tilted slightly (about 7°), but the potential energy surface is very flat as a function of the tilting angle. The present results are similar to the calculations by Kokalj et al. [17,18] for N_2O on Pd(110). The adsorbed N_2O molecule undergoes hardly any distortion ($d_{N–N} = 1.15$ Å and $d_{N–O} = 1.21$ Å) as compared with the calculated N–N and N–O distances in the free molecule, 1.15 and 1.21 Å, respectively, which indeed are in good agreement with the experimentally determined values (1.127 Å for $d_{N–N}$ and 1.185 Å for $d_{N–O}$) [44].

Interaction of N_2O through the terminal N_t atom with other positions on the surface is negligible (-0.05 eV $< E_{ads} < 0.05$ eV), indicating that the displacement of the adsorbed N_2O molecule on the surface will lead to its spontaneous desorption.

Other stable structures of adsorbed N_2O originate from interactions between the two N atoms and the surface. The most stable configuration occurs when the N_t atom is in bridging position and the N_c atom is in top position, with an adsorption energy of -0.31 eV. In this case, the molecule is distorted; the N–N–O angle is 123°. The variation of the N–N distance is important (1.35 Å) as compared with that in gas-phase N_2O (1.15 Å). In contrast, the N–O distance remains very similar (1.22 Å). Hence, as the N–N bond is largely activated whereas the N–O bond is not distorted, this adsorption mode is considered a suitable starting point for the dissociation of the N_2O molecule into adsorbed NO and N species.

The adsorption via the two terminal atoms (N_t and O) is also stable. An adsorption energy of -0.30 eV is computed when the two terminal atoms are in top position. Once again, the geometry of the adsorbed molecule is very different from

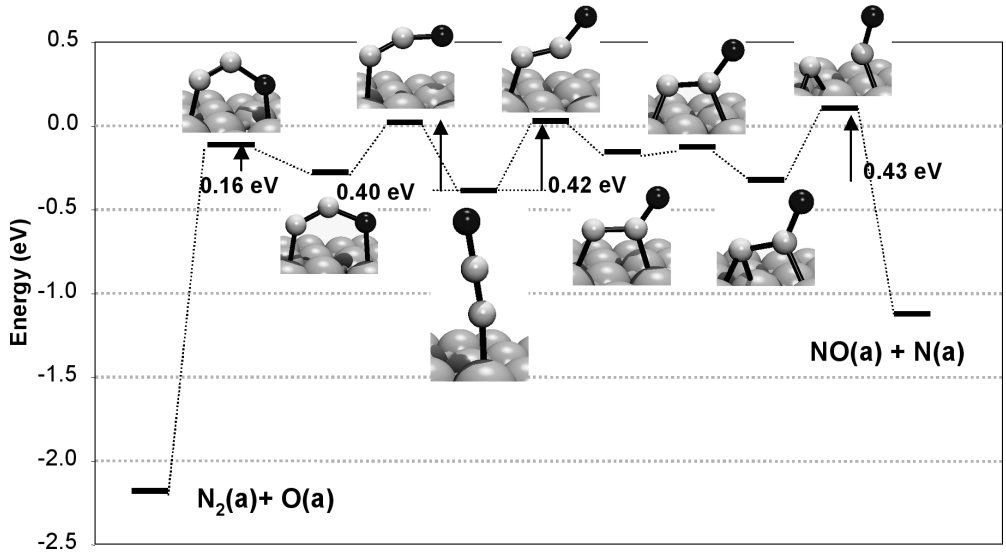

Fig. 6. Reaction paths for N_2O activation and decomposition into adsorbed $N_2 + O$ and $NO + N$. The zero energy level corresponds to the non-interacting surface and N_2O in the gas phase.

the geometry in the gas phase. The angle N–N–O is 128° and the associated N–O (1.32 Å) and N–N (1.20 Å) distances are significantly larger compared with those in gas-phase N_2O. In this case the activation of the N–O bond is more important than the activation of the N–N bond, and this adsorption mode can be the starting point for the dissociation into N_2 and O species. Therefore, Rh(111) can activate both the N–N and the N–O bonds of the N_2O molecule when flat, bidentate, adsorption modes are considered. Accordingly, the first step for N_2O decomposition should involve the transformation of the top adsorption mode into flat adsorption modes.

On oxide surfaces, the most stable adsorption mode is via the O atom, which leads to spontaneous N_2 desorption. For Rh(111), any attempt to start from N_2O adsorbed via O leads to desorption, and the direct transposition, characteristic of oxides, does not take place. In order to confidently exclude this possibility, we have computed the adsorption energy for N_2O adsorbed via O in top position for a fixed Rh–O distance. For Rh–O distances around 2.0 Å, the values of the N–N and N–O distances do not change with respect to the gas-phase molecule, and the adsorption energy is positive (0.4 eV for 2.13 Å and 0.6 eV for 2.03 Å, respectively). These results allow us to rule out this adsorption mode.

3.2.2. N_2O dissociation

Starting from the more stable N_2O adsorption mode, two possible pathways stemming from N_2O dissociation have been modeled. The overall reaction path for N_2O decomposition on Rh(111) to give adsorbed $N_2 + O$ or $NO + N$ is shown schematically in Fig. 6, in which we have also displayed the transition states and intermediate adsorbate structures. Both processes are exothermic, particularly the path leading to $N_2 + O$. The activation energy is 0.4 eV, which is very similar to the barrier computed for Pt(111) [22]. Starting from the most stable N_2O adsorption mode, two transition states of about 0.4 eV must be overcome to originate adsorbed $NO + N$. Hence, both thermodynamically and kinetically, the favored decomposition process of N_2O corresponds to the formation of N_2 and not that of NO. Since the adsorption energy of N_2 on the surface is very low, it desorbs rapidly, leading to a high oxygen coverage on the surface, in agreement with experimental observations. On the other hand, the adsorption energy of NO (~ -2.0 eV) [45] is higher than the activation energy for N_2O formation.

Fig. 6 can also be used to explain the production of molecular nitrogen at relatively high temperatures in the reduction of NO by CO on Rh(111) via the formation and subsequent decomposition of an N–NO surface intermediate [27,28]. Although the present activation barrier for the reaction $NO(ads) + N(ads) \rightarrow N_2O(ads)$ on Rh(111) is relatively high (1.33 eV), it is lower than the theoretical value predicted by Burch et al. [20] of 1.78 eV. They ruled out this mechanism at low temperatures and speculated on the possibility of an alternative pathway involving a dimer $(NO)_2$ species. This possibility was also explored by Bogicevic and Hass [21] on Cu(111) and Pt(111), who concluded that the dimer route is not possible on Pt(111). In the present study, the computed activation barrier for the formation of N_2 from adsorbed N atoms is 2.10 eV. Although these data have to be taken cautiously, since the interaction between co-adsorbed species is not considered and coverage effects may change the energy profile, it is reasonable to state that N_2O formation is preferred over N_2 formation if both NO and N species are present on the surface. This supports the recent study [29] on the formation of N_2O and N_2 in a steady-state $NO + CO$ reaction on Pd(110), which concluded that the pathway through the intermediate adsorbed N_2O prevails be-

low 600 K, whereas the associative desorption of nitrogen atoms dominates at higher temperatures.

The present results also provide theoretical support for a suggestion by Zaera and Gopinath [28], who stated that the most likely way for the undissociated NO to participate in molecular nitrogen formation is via the formation and subsequent decomposition of an N–NO surface intermediate.

4. Conclusions

Density functional theory calculations elucidate molecular aspects of different catalytic processes involving N-containing species on Rh(111).

- It has been shown that CN formation from adsorbed C and N atoms is preferred over N_2 recombination. The formation of HCN via CH fragments reacting with adsorbed N atoms is energetically favored, supporting previous experimental findings.
- The processes of N_2O dissociation into $N_2 + O$ or $NO + N$ are both exothermic on Rh(111), although the former is preferred thermodynamically. In addition, the energy barriers of the pathway toward adsorbed N_2 and O are slightly lower than those toward adsorbed $NO + N$. Therefore, it is concluded that N_2 is the main reaction product, in agreement with experimental results over Rh catalysts. Our results also support the conclusion that N_2O can be formed as a reaction intermediate during the reduction of NO to N_2 over rhodium, by reaction between adsorbed NO and N atoms.

Acknowledgments

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References

[1] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994.
[2] R.I. Masel, Principles of Adsorption and Reaction on Solid Surfaces, Wiley, New York, 1996.
[3] F. Zaera, Prog. Surf. Sci. 69 (2001) 1.
[4] R.A. van Santen, M. Neurock, Catal. Rev.-Sci. Eng. 37 (1995) 557.
[5] R.A. van Santen, J.W. Niemantsverdriet, Chemical Kinetics and Catalysis, Plenum, New York, 1995.
[6] R.D. Cortright, J.A. Dumesic, Adv. Catal. 46 (2001) 161.
[7] A. Gross, Surf. Sci. 500 (2002) 347.
[8] F. Illas, C. Sousa, J.R.B. Gomes, A. Clotet, J.M. Ricart, in: M.A. Chaer-Nascimento (Ed.), Theoretical Aspects of Heterogeneous Catalysis, Progress in Theoretical Chemistry and Physics, vol. 8, Kluwer Academic Publishers, Dordrecht, 2001, pp. 149–181.
[9] C.J.H. Jacobsen, S. Dahl, B.S. Clausen, S. Bahn, A. Logadottir, J.K. Nørskov, J. Am. Chem. Soc. 123 (2001) 8404.
[10] R.M. van Hardeveld, A.J.G.W. Schmidt, R.A. van Santen, J.W. Niemantsverdriet, J. Vac. Sci. Technol. A 15 (1997) 1642.
[11] R.M. van Hardeveld, R.A. van Santen, J.W. Niemantsverdriet, J. Phys. Chem. B 101 (1997) 7901.
[12] E. Herceg, M. Trenary, J. Am. Chem. Soc. 125 (2003) 15758.
[13] F. Ample, J.M. Ricart, A. Clotet, D. Curulla, J.W. Niemantsverdriet, Chem. Phys. Lett. 385 (2004) 52.
[14] N. Macleod, J. Isaac, R.M. Lambert, J. Catal. 193 (2000) 115.
[15] F. Kapteijn, J. Rodríguez-Mirasol, J.A. Moulijn, Appl. Catal. B 9 (1996) 25.
[16] J. Pérez-Ramírez, F. Kapteijn, G. Mul, X. Xu, J.A. Moulijn, Catal. Today 76 (2002) 55.
[17] A. Kokalj, I. Kobal, H. Horino, Y. Ohno, T. Matsushima, Surf. Sci. 506 (2002) 196.
[18] A. Kokalj, I. Kobal, T. Matsushima, J. Phys. Chem. B 107 (2003) 2741.
[19] A. Kokalj, Surf. Sci. 213 (2003) 532.
[20] R. Burch, S.T. Daniells, P. Hu, J. Chem. Phys. 117 (2002) 2902.
[21] A. Bogicevic, K.C. Hass, Surf. Sci. 506 (2002) L237.
[22] R. Burch, S.T. Daniels, J.P. Breen, P. Hu, J. Catal. 224 (2004) 252.
[23] J.F. Paul, J. Pérez-Ramírez, F. Ample, J.M. Ricart, J. Phys. Chem. B 108 (2004) 17921.
[24] V.P. Zhdanov, B. Kasemo, Surf. Sci. Rep. 29 (1997) 31.
[25] D.N. Belton, C.L. DiMaggio, K.Y.S. Ng, J. Catal. 144 (1993) 273.
[26] D.N. Belton, C.L. DiMaggio, S.J. Schmieg, K.Y.S. Ng, J. Catal. 157 (1995) 559.
[27] F. Zaera, C.S. Gopinath, Chem. Phys. Lett. 332 (2000) 209.
[28] F. Zaera, C.S. Gopinath, J. Mol. Catal. A 167 (2001) 23.
[29] Y. Ma, I. Rzeznicka, T. Matshushima, Chem. Phys. Lett. 338 (2004) 201.
[30] E.V. Kondratenko, J. Pérez-Ramírez, Catal. Lett. 91 (2003) 211.
[31] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
[32] G. Kresse, J. Hafner, Phys. Rev. B 48 (1993) 13115.
[33] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
[34] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[35] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
[36] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[37] G. Henkelman, B.P. Uberuaga, H. Jónsson, J. Chem. Phys. 113 (2000) 9901.
[38] F. Ample, A. Clotet, J.M. Ricart, Surf. Sci. 448 (2004) 111.
[39] W. Daum, F. Dederichs, J.E. Muller, Phys. Rev. Lett. 80 (1998) 766.
[40] H. Yang, T. Caves, J.L. Whiten, J. Chem. Phys. 103 (1995) 8756.
[41] G.L. Beltramo, T.E. Shubina, S.J. Mitchell, M.T.M. Koper, J. Electroanal. Chem. 563 (2004) 111.
[42] A. Michaelides, P. Hu, J. Chem. Phys. 114 (2001) 5792.
[43] A. Michaelides, Z.-P. Liu, C.J. Zhang, A. Alavi, D.A. King, P. Hu, J. Am. Chem. Soc. 125 (2003) 3704.
[44] J.-L. Teffo, A. Chendin, J. Mol. Spectrosc. 138 (1989) 134.
[45] D. Loffreda, D. Simon, P. Sautet, Chem. Phys. Lett. 291 (1998) 15.