Catalysis Today 154 (2010) 118–126

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

A novel mechanism for spectator CO-mediated reaction with unique *cis*-$(NO)_2$ dimer on a Co^{2+}-dimer/γ-Al_2O_3(1 1 0) model catalyst: Density functional theory calculations

Toshiaki Taniike[a,1], Mizuki Tada[a,2], Rudy Coquet[a], Yoshitada Morikawa[b],
Takehiko Sasaki[c], Yasuhiro Iwasawa[a,*]

[a] *Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[b] *The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[c] *Department of Chemistry, Graduate School of Frontier Science, The University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan*

ARTICLE INFO

Article history:
Available online 8 April 2010

Keywords:
Density functional theory calculation
γ-Al_2O_3(1 1 0) surface structure
Supported Co catalyst
NO adsorption
cis-$(NO)_2$ dimer
Spectator CO
NO–CO reaction
Reaction mechanism

ABSTRACT

Density functional theory calculations for NO adsorption and NO–CO reaction on a Co^{2+}-dimer/γ-Al_2O_3(1 1 0) model catalyst were conducted to understand two new aspects of the increases in the amount and reduction rate of adsorbed NO by gas phase CO molecules which are undetectable at the Co^{2+}-ensemble/γ-Al_2O_3 catalyst surface. Three kinds of dinitrosyl adsorbates were found and assigned to normal *gem*-dinitrosyl species (*gem*-dinitosyl I and II) and an unique *cis*-$(NO)_2$ dimeric species. The *gem*-dinitrosyl II with a reconstructed structure involving Co–O_{surf} cleavage was considered as stable species experimentally observed, which is responsible for the spectator CO-promoted NO adsorption. We also found that the *cis*-$(NO)_2$ dimeric species specific for the Co^{2+}-ensemble structure possesses a much higher reactivity than the *gem*-dinitrosyl species, enabling the facile reaction with CO that is very weakly trapped at the surface. In the *cis*-$(NO)_2$ dimeric species two adsorbed NO molecules on two adjacent Co^{2+} sites interact with each other due to the opposed orientation of the unoccupied *d* orbitals of the two Co^{2+}, resulting in easy formation of a N–N bond through the $2\pi^*$–$2\pi^*$ hybridization. The NO adsorbates modify and activate the surface (Co^{2+} sites) to make pseudo-compounds (intermediates) with CO at the Co^{2+} sites in such a way that CO is not detected at the surface. The potential energy surface for the NO–CO reaction is presented and the transition states and intermediates are discussed.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Ensemble catalysts with concerted metal ion sites often exhibit characteristic catalysis, which may not be performed by a single metal site [1–11]. We found a new phenomenon that the catalytic reduction and adsorption of NO on a Co^{2+}-ensemble/γ-Al_2O_3 catalyst were significantly promoted by gas phase CO undetectable at the catalyst surface [7,12–15]. The Co^{2+}-ensemble/γ-Al_2O_3 catalyst was prepared by chemical vapor deposition (CVD) of $Co_2(CO)_8$ on γ-Al_2O_3, followed by step-by-step treatments in a controllable manner, and characterized by EXAFS, diffuse reflectance UV/vis, FT-IR, Raman, TPD, etc [15–17]. The CVD Co^{2+}-ensemble/γ-Al_2O_3 catalyst thus obtained was *ca.* 50 times more active for $2NO + CO \rightarrow N_2O + CO_2$ than a usual impregnated Co^{2+}/γ-Al_2O_3 catalyst. The new aspect "surface catalytic reaction and adsorption assisted by gas phase molecules" is briefly summarized as follows. NO adsorbs to give paired peaks at 1769 and 1849 cm^{-1}, which may be considered as a *gem*-dinitrosyl species ($Co^{2+}(NO)_2$), while CO stays on the surface as shortly as *ca.* 10^{-10} s and its adsorbed amount is so small as undetectable volumetrically and IR-spectroscopically below their detection limits. Most of heterogeneous catalytic reactions are known to follow the Langmuir–Hinshelwood (LH) mechanism requiring the adsorption-mediated activation of reactant molecules rather than the Eley–Rideal (ER) mechanism which is induced by the collisional energy of impinging molecules from the gas phase. However, CO which rarely resides on the catalyst surface significantly promotes the reactivity of adsorbed NO to produce N_2O according to TPD of adsorbed NO. Further, the presence of CO in the gas phase also increases the equilibrium amount of NO adsorbed at the surface by

---

* Corresponding author. Present address: Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan. Tel.: +81 42 443 5921; fax: +81 42 443 5483.
E-mail addresses: iwasawa@pc.uec.ac.jp, iwasawa@chem.s.u-tokyo.ac.jp (Y. Iwasawa).

[1] Present address: School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292, Japan.

[2] Present address: Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan.

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.048

ca. 2 times. Interestingly, a Co^{2+}-monomer/γ-Al_2O_3 catalyst prepared in a similar way to the Co^{2+}-ensemble/γ-Al_2O_3 catalyst had no activity for the same reaction and never showed the spectator CO-promoted NO adsorption, in spite of the similarity in the electronic state and local structure of their Co^{2+} sites [15]. Thus, the new surface phenomenon promoted by gas-phase CO molecules may originate from the Co^{2+}-ensemble structure. Importance of a synergistic cooperation between nearby Co^{2+} sites was also indicated to enhance the catalytic activity of the selective NO reduction on Co^{2+}/ferrierite catalysts [18,19]. However, it is hard to find experimentally the key issue and detailed mechanism for the surface event assisted by gas phase molecules because CO is neither spectroscopically nor volumetrically detectable at the surface under the reaction conditions.

Recently, we proposed a surface structure of a Co^{2+}-dimer/γ-Al_2O_3(1 1 0) model catalyst based on the experimental characterizations and density functional theory (DFT) calculations [20], and suggested that an adsorbate–adsorbate interaction imposed by the opposed orientation of the unoccupied *d* orbitals of the adjacent Co^{2+} ions may be the origin of the new catalytic phenomenon on the Co^{2+}-ensemble catalyst [15,21]. By means of the DFT calculations closely compared with our recent experimental results [15], here we report that a *cis*-$(NO)_2$ dimeric species through the adsorbate–adsorbate interaction is the origin of the high activity of the Co^{2+}-ensemble/γ-Al_2O_3 catalyst, and that this highly reactive *cis*-$(NO)_2$ dimer enables the reaction with only weakly adsorbed, namely chemically unactivated CO molecules. We also suggest that the CO-promoted NO adsorption may be correlated with the appearance of a new *gem*-dinitrosyl species accompanied with CO-induced cleavage of a Co–O_{surf} bond at the interface.

2. Calculation

The density functional theory (DFT) at the level of generalized gradient approximation (GGA) [22] has been employed throughout calculations. The exchange–correlation functional was of Perdew–Burke–Ernzerhof (PBE) [23]. The basis set was the double numeric basis with polarization functions (DNP) [24], whose accuracy is comparable to the famous 6-31G** basis. The core parts were described by the effective core potentials (ECP) of Dolg et al. [25,26]. These calculations were conducted by the DMOL3 program package [24]. The catalyst surface was modeled by a repeated slab separated by a *ca.* 1-nm vacuum region. The *k*-point mesh was $3 \times 4 \times 1$ (the size of the unit cell was 0.79110, 0.55939 and 1.90503 nm, which had been decided in the previous calculations [20]). The convergence criterion for SCF calculations was 1.0×10^{-5} Hartree and those for geometry optimization were 2.0×10^{-5} Hartree in energy and 2.1×10^{-3} Hartree/Bohr in force.

The vibrational frequencies of adsorbates were calculated in a way that force constants, second-order derivatives of energy were approximated by a numerical differentiation, where each atom was displaced from the equilibrium position by 0.001 nm in the *x*, *y*, and *z* directions. In addition, we used a partial hessian consisting of the force constants of a Co^{2+} dimer and adsorbates, which accurately reproduced the vibrational frequencies obtained by diagonalizing a total hessian.

Transition state searches were executed as follows. At first, the linear synchronous transit method (LST) [27] was used to search the energy maximum in the line connecting a reactant and product. From this approximate energy maximum, energy minimization in the direction conjugate to the reaction pathway (CG) was conducted. Then the quadratic synchronous transit method (QST) was used to improve the energy maximum point. Finally the CG/QST cycle was repeated until the gradient at the transition state decreased within 5.3×10^{-3} Hartree/Bohr. The obtained transition state was refined in order to give a sole imaginary frequency for the reaction coordinate. Further, we confirmed whether the obtained transition state corresponded to the maximum in the reaction pathway or not by additional LST/QST/CG calculations between the reactant (product) and the transition state.

As was described in the previous calculations [20], each Co^{2+} ion had a high spin state, i.e. $Co^{2+}(\uparrow\uparrow\uparrow)$ and the relative spin orientation of the adjacent Co^{2+} ions ($Co^{2+}(\uparrow\uparrow\uparrow)\cdots Co^{2+}(\uparrow\uparrow\uparrow)$ or $Co^{2+}(\uparrow\uparrow\uparrow)\cdots Co^{2+}(\downarrow\downarrow\downarrow)$) did not affect the energy and structure of the catalyst model. Because CO does not have any unpaired electron, CO adsorption was totally independent of the spin orientation of the adjacent Co^{2+} ions. NO with one unpaired electron in a $2\pi^*$ orbital is known to makes its doublet anti-parallel to the spin of Co^{2+} ($Co^{2+}(\uparrow\uparrow\uparrow)$–$NO(\downarrow)$) [28], and as for the relative preference we confirmed that the anti-parallel orientation was 0.25 eV more stable than the parallel orientation. In addition, bridging NO adsorbates, which emerged in mononitrosyl or geminal species as a result of the underestimated Co–N bond length (described later), always favored the $Co^{2+}(\uparrow\uparrow\uparrow)$–$NO(\downarrow)$–$Co^{2+}(\uparrow\uparrow\uparrow)$ spin configuration than $Co^{2+}(\uparrow\uparrow\uparrow)$–$NO(\downarrow)$–$Co^{2+}(\downarrow\downarrow\downarrow)$ by 0.2–0.3 eV. Therefore, we fixed the total spin at $6 - x$ in a system which included x NO adsorbates ($x = 0$–2). Such restriction to the total spin density gives correct spin states on metal ions, compared to spin-unrestricted calculations [29].

In our calculations, a Co^{2+} dimer composed of the two adjacent Co^{2+} ions weakly interacted with each other significantly prevented a SCF cycle from converging because multiple *d* orbitals underlay in a narrow energy region. For this convergence problem, we employed the following scheme [20] using the thermal smearing method [30]. Firstly, a single-point calculation with a high smearing temperature, 0.010 Hartree was done. Next the obtained electronic state was re-converged with a milder smearing rate, 0.008 Hartree. In this way, the smearing rate was gradually decreased to 0.004 Hartree, which was enough small to evaluate accurate energies and frequencies (the error ranges which were derived from calculations about several dinitrosyl-Co^{2+} complexes, were 0.05–0.10 eV for the energy and 10–20 cm^{-1} for the frequency).

The interaction between NO and highly correlated metal or metal ions is one of the major challenges of DFT with pure functionals such as PBE. In our system, the adsorption energy of mononitrosyl species bridging the two adjacent Co^{2+} ions was overestimated as largely as by *ca.* 1.5 eV, and its vibrational frequency was greatly red-shifted by 180 cm^{-1}, indicating an overestimated back-donation from Co^{2+} to NO. Similar problems of the pure-functional DFT have been reported for CO adsorption on a Pd(1 1 1) surface [31,32], CO and NO adsorption on a strongly correlated NiO(1 1 0) surface [29,33,34], and so on. These problems partly come from the well-known fact that the pure-functional DFT underestimates the gap size between valence and conduction bands (or orbitals) [35]. The underestimation of the HOMO-LUMO gap size of NO in the pure-functional DFT results in an overestimated back-donation into the unoccupied $2\pi^*$ orbital of NO, which leads to the increase of adsorption energies, red-shift of the vibrational frequencies, and elongation of the N=O bond length. Since the degree of the error depends on the kind of the adsorption sites and the number of the metal ions bound to NO, we did not compare the relative stability of various NO adsorbates at different sites and adsorption modes. Another source of the problems is the incorrect description of the on-site Coulomb repulsion [29], which causes spin overmixing between a highly correlated metal ion and NO, i.e. shrinks and strengthens the Co^{2+}–N bond. In spite of these problems, however, it is known that the activation barrier for the N–O scission is much more accurate due to the error cancellation [36,37]. Similarly, we confirmed that the difference between the asymmetric and symmetric vibration frequencies of dinitrosyl

Download English Version:

https://daneshyari.com/en/article/56681

Download Persian Version:

https://daneshyari.com/article/56681

Daneshyari.com