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Reaction mechanism of methyl nitrite dissociation during co catalytic coupling to dimethyl oxalate: A density functional theory study☆

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ABSTRACT

Dissociation of methyl nitrite is the first step during CO catalytic coupling to dimethyl oxalate followed by hydrogenation to ethyl glycol in a typical coal to liquid process. In this work, the first-principle calculations based on density functional theory were performed to explore the reaction mechanism for the non-catalytic dissociation of methyl nitrite in the gas phase and the catalytic dissociation of methyl nitrite on Pd(111) surface since palladium supported on alpha-alumina is the most effective catalyst for the coupling. For the non-catalytic case, the calculated results show that the CH_3O–NO bond will break with a bond energy of 1.91 eV, and the produced CH_3O radicals easily decompose to formaldehyde, while the further dissociation of formaldehyde in the gas phase is difficult due to the strong C–H bond. On the other hand, the catalytic dissociation of methyl nitrite on Pd(111) to the adsorbed CH_3O and NO takes place with a small energy barrier of 0.03 eV. The calculated activation energies along the proposed reaction pathways indicate that (i) at low coverage, a successive dehydrogenation of the adsorbed CH_3O to CO and H is favored while (ii) at high coverage, hydrogenation of CH_3O to methanol and carbonylation of CH_3O to methyl formate are more preferred. On the basis of the proposed reaction mechanism, two meaningful ways are proposed to suppress the dissociation of methyl nitrate during the CO catalytic coupling to dimethyl oxalate.

1. Introduction

Ethylene glycol (EG), a crucial chemical raw material with a global demand of about 25 million tons each year, is primarily used in polyester manufactures or antifreezing fluid production [1–3]. At present, the universal industrial approach to produce EG is from ethylene oxidation based on petroleum resource. However, due to the shrink of oil resources and the continuous increase of EG demand, an alternative EG synthesis technology called coal to ethylene glycol (CTEG) has attracted substantial attention [1,4–6]. CO catalytic coupling with methyl nitrite (MN) to dimethyl oxalate (DMO) is the crucial step in the conversion of inorganic C1 to organic C2 in CTEG, and thus it is considered to be one of the most important applications in C1 chemistry [5]. The coupling reaction can be expressed as,

$$2CH_3ONO + 2CO \rightarrow (COOCH_3)_2 + 2NO. \quad (1)$$

Hydrogenation of DMO produces EG. The most effective catalysts for the coupling reaction are the supported Pd catalysts. However, under the coupling reaction conditions, the non-catalytic (thermal) decomposition of MN in the gas phase to produce methanol (ME) and formaldehyde and the catalytic dissociation of MN on Pd catalysts to yield ME and methyl formate (MF) are two important side reactions of the coupling reaction [7,8], which can be expressed as follows,

$$2CH_3ONO \rightarrow CH_3OH + CH_2O + 2NO \quad (2)$$

$$4CH_3ONO \rightarrow CHOOCH_3 + 2CH_3OH + 4NO. \quad (3)$$

However, the detailed reaction mechanism for these two side reactions, especially at the atomistic level, remains unclear. In order to suppress the dissociation of MN and thus improve the selectivity of DMO in the coupling reaction, it is therefore of vital importance to address the reaction mechanism. In this contribution, we report extensive density functional theory (DFT) investigations to explore the reaction mechanism for both non-catalytic dissociation of MN in the gas phase and catalytic dissociation of MN on Pd(111) surface.

Methyl nitrite (CH_3ONO, MN) is a very reactive molecule in the gas phase because of its weak O–NO bond (the bond energy is 1.82 eV). The O–NO bond would be further weakened upon adsorption on the

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active metal surfaces, owing to the surface stabilization of the adsorbed methoxy (CH_3O) and NO [9,10]. Hence, MN can be used as the adsorbed precursors for the preparation of CH_3O intermediates on a number of metal surfaces. Experimentally, He and co-workers studied the thermal dissociation of MN in a static reactor at temperatures in the range 450–520 K [11]. The products monitored by Fourier Transform Infrared Spectroscopy and gas–liquid chromatography included ME, formaldehyde, nitric oxide, and carbon monoxide. Their results showed that the initial O–N bond scission is pressure-dependent in the investigated temperature and pressure ranges. The dissociation of MN on metal surfaces has also been investigated by several groups [7–10,12]. Peck and co-workers performed auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) studies on MN dissociation on Pt(111) and Pt–Sn alloys [9,10]. They found that the activation of MN is very facile to produce adsorbed CH_3O and NO, and the adsorbed CH_3O could be either decomposed to CO and H or hydrogenated to ME, depending on the initial coverage of MN. At low coverage of MN ($\theta_{MN} < 0.15$ Monolayer (ML)), the surface reactivity is the highest and the reactions during TPD only produce gas phase CO, H_2, and NO. However, at higher coverages, as the concentrations of co-adsorbates increase, the surface is deactivated and the gas phase ME is an important product. Nevertheless, the main pathway for CH_3O on Pt(111) is complete dehydrogenation to form CO and H_2. By contrast, the dissociation of CH_3O on the Pt–Sn alloys yields formaldehyde and adsorbed hydrogen that efficiently hydrogenates CH_3O to form ME [9,10]. Zhuo and Jiang investigated the vapor phase catalytic dissociation of MN on several supported Pd catalysts [7,8]. They found that the catalytic activities were ranked in the following order: Pd/γ-Al_2O_3 > Pd/AC > Pd/α-Al_2O_3 > Pd–Ti/α-Al_2O_3, and the acidic supports such as HY zeolite, γ-Al_2O_3 and SiO_2 also exhibited moderate activity for the dissociation of MN. As a result, they suggested that the dissociation of MN on acidic support is an attractive approach to synthesize MF [7,8]. On the basis of the experimental observations, they proposed a possible successive dehydrogenation mechanism. However, the detail reaction mechanism at atomistic level remains unclear. Our group also investigated the thermal dissociation of MN in the gas phase and the catalytic dissociation of MN on a Pd/α-Al_2O_3 catalyst [12]. It is found that the thermal dissociation of MN would produce ME, formaldehyde, and NO while the catalytic dissociation of MN mainly produced ME, MF and NO.

To the best of our knowledge, little theoretical work has been devoted to exploring the reaction mechanism for the dissociation of MN in the gas phase and on transition metal surfaces. By means of DFT calculations, Gomes *et al.* investigated the adsorption of MN on Au(111) surface, and found that only the cis-conformer is present on the Au surface [13]. Although the theoretical work that related to the MN on transition metal surfaces is limited, the chemisorption and reactivity of the dissociative species, *i.e.*, CH_3O on transition metal surfaces have been extensively studied by DFT calculations [14–17]. For example, Chen and co-workers systematically investigated the CH_3O dissociation pathways on Pd(111), Cu(111), and Pd–Zn alloyed surfaces using periodic DFT calculations. They found that the activation energies for C–O scission of CH_3O species on all the three surfaces are 0.93–1.14 eV higher than the corresponding barriers for C–H bond breaking, implying that C–H breaking is clearly favored than C–O cleavage. Moreover, the dehydrogenation of CH_3O to CH_2O is a very facile reaction on Pd(111) according to the calculated energy barrier and reaction energy. After that, the same group continues to investigate the dehydrogenation of formaldehyde (CH_2O) and formal (CHO) on Pd(111), Cu(111), and Pd–Zn alloyed surfaces [18]. Their calculated results convincingly demonstrated that complete dehydrogenation of CH_2O to CO on Pd(111) is both thermodynamically and kinetically favorable, but unfavorable on Cu, and Pd–Zn alloyed surfaces [18]. Likewise, Jiang *et al.* investigated ME dehydrogenation to CO and H_2 on Pd(111) using DFT [16]. On the basis of the calculated adsorption energies and activation energies, they suggested that (i) desorption rather than dehydrogenation is preferable for the adsorbed ME due to the weak interaction of ME with the Pd surface. (ii) For the adsorbed CH_2O, the possibilities for desorption and dehydrogenation are comparable according to the similar adsorption energy and dehydrogenation activation barrier. (iii) For other species, dehydrogenation is more favorable due to the strong adsorptions.

It is clear from the previous theoretical work that CO and H_2 are readily formed from the dehydrogenation of the adsorbed CH_3O on Pd surface. Meanwhile, MN is very facile to decompose to adsorbed CH_3O and NO due to the considerably weak CH_3O–NO bond. Consequently, one may easily deduce that CO, H_2, and NO are the main products for the dissociation of MN on Pd catalysts. This reasonable suspect is, however, inconsistent with the experimental observations on Pd catalysts where ME and MF are the main products for the catalytic dissociation of MN on Pd catalysts (see Eq. (3)) [7,8,12]. Obviously, the reaction mechanism for the dissociation of MN on Pd catalyst is different from that of dissociation of ME or the adsorbed CH_3O species. In order to provide a better understanding of the MN dissociation reactions on Pd catalysts as well as the non-catalytic dissociation of MN in the gas phase, we report extensive DFT calculations in this contribution to explore the reaction mechanism for MN dissociation on Pd(111) surface and in the gas phase at atomistic level, aiming to shed light on the reaction pathways at different conditions and the origin of the different product distribution between the non-catalytic and catalytic dissociation of MN.

2. Computational Details

In this work, all the DFT calculations were performed with the VASP code [19–22], in which the wave functions at each k-point are expanded with a plane wave basis set with a kinetic cutoff energy up to 400 eV. The interactions between valence electrons and ion cores were treated by Blöchl's all-electron-like projector augmented wave (PAW) method [23,24]. The exchange-correlation functional utilized was the generalized gradient approximation functional proposed by Perdew, Burke, and Ernzerhof, known as GGA-PBE [25]. Brillouin zone sampling was performed using a Monkhorst-Pack grid [26] and electronic occupancies were determined according to a Methfessel–Paxton scheme with an energy smearing of 0.2 eV [27]. The calculated lattice constant for bulk Pd is 0.395 nm, which is in reasonable agreement with the experimental value [28] (0.389 nm) and previous theoretical results [29,30].

A $p(2 \times 2)$ unit cell was utilized to model the Pd(111) surface, achieving a surface coverage of 0.25 ML for the adsorbates. The (111) surfaces were modeled by the repeated three-layer slabs separated by a vacuum layer as large as 1.2 nm along the direction of the surface normal to avoid the periodic interactions. Our previous work showed that increasing the thickness of the slab had negligible effect on the adsorption energies [31]. The first Brillouin zone of the $p(2 \times 2)$ unit cell was sampled with Γ-centered $7 \times 7 \times 1$ *k*-point grids, which were proven to be sufficient for this cell [31]. The bottom two layers in the slab models were fixed and the topmost layer and the adsorbates were allowed to relax during geometry optimization. The dipole corrections were found to have negligible effect on the adsorption energies, and therefore were not considered in this work. The zero point energy (ZPE) corrections were not included in this work.

The dimer method was used to locate the transition states (TSs) for the elementary reactions. This method has been described in detail elsewhere [32]. In all the calculations, a force-based conjugated-gradient method [33] was used to optimize the geometry. Saddle points and minima were considered to be converged when the maximum force in every degree of freedom was less than 0.3 $eV \cdot nm^{-1}$. In order to obtain accurate forces, the total energy and band structure energy were converged to within 1×10^{-7} eV/atom during the electronic optimization. To verify the adsorption configurations and TSs, vibrational frequency calculations were carried out. The Hessian matrix was determined by the numerical finite difference method with a step size of 0.002 nm for the displacement of the individual atoms of the adsorbates