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Insights into the mechanism of nitrobenzene reduction to aniline over Pt catalyst and the significance of the adsorption of phenyl group on kinetics

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HIGHLIGHTS

- Selective catalysis of the desired functional group of aromatic molecules explained.
- Nitrobenzene reduction to aniline over Pt modeled by first principles calculation.
- Double H-induced path identified as the most favorable route for activating the $-NO_2$ group.
- Adsorption of the phenyl group affected considerably the kinetic barrier.

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ABSTRACT

Aniline ($C_6H_5NH_2$) plays a significant role in both industry and daily life, and can be synthesized via catalytic hydrogenation of nitrobenzene ($C_6H_5NO_2$) over transition metals; however fundamental investigations on reaction mechanisms in the heterogeneous catalysis are still lacking. In this work, the nitrobenzene reduction reaction over the Pt(1 1 1) model catalyst was studied using density functional theory (DFT) with the inclusion of van der Waals interaction, for fundamentally understanding the mechanisms at atomic and molecular levels. It was found that the double H-induced dissociation of N-O bond was the preferential path for the activation of nitro group, having a much lower reaction barrier than that of the direct dissociation and single H-induced dissociation paths. The overall mechanisms have been identified as: $C_6H_5NO_2^* \rightarrow C_6H_5NOOH^* \rightarrow C_6H_5N(OH)_2^* \rightarrow C_6H_5NOH^* \rightarrow C_6H_5NHOH^* \rightarrow C_6H_5NH^* \rightarrow C_6H_5NH_2^*$. The overall barrier of the nitro group reduction was calculated to be 0.75 eV, which is much lower than that of the benzene reduction (1.08 eV). Our DFT data elucidates clearly the reason why the major product of nitrobenzene reduction reaction was aniline. Furthermore, the adsorption/desorption of phenyl group was found to have significant impacts on kinetic barriers. Generally, in the hydrogenation process (N-H or O-H bond association), the phenyl group preferred to adsorb on the surface; but in the dissociation process (N-O bond dissociation) it preferred to desorb transiently at the transition state and to adsorb again when the dissociation was completed. This study also provides a solid theoretical insight into the selective catalysis of the large aromatic compounds.

1. Introduction

Aniline ($C_6H_5NH_2$) is an important chemical raw material, which is widely used in the rubber, fine chemicals (dyes and pigments), agrochemical (pesticides and herbicides) and pharmaceutical industry [1–13]. Aniline is manufactured via catalytic hydrogenation of nitrobenzene ($C_6H_5NO_2$) over a series of transitional metal catalysts such as Pd, Pt, Ni, Cu, Ru and Au, at various conditions, e.g., gas-phase or liquid-phase hydrogenation, as well as electrochemical reduction [1–13]. In the catalytic hydrogenation of nitrobenzene, the nitro group is usually reduced to amino group but the phenyl group remains [1–13]. A wide range of catalysts for

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reduction of nitrobenzene to aniline have been studied experimentally. Among them, noble Pt and Pd based catalysts were identified to be highly effective under modest conditions [6,10,14–20]. Most of the investigations have been focused on the catalytic performance but not on the mechanisms. The mechanisms of the nitrobenzene reduction are complicated and the reaction environments could play significant roles, for instance, the products are different under acidic, neutral and alkaline electrochemical conditions [2,4]. Gelder et al. and Corma et al. proposed some insights into the mechanisms in the nitrobenzene reduction [12,13]. In fact, with respect to the aromatic compounds having multiple functional groups, the selectivity towards the desired functional group reaction is a big challenge in heterogeneous catalysis. For example, in the reduction of halonitrobenzene, to achieve a selective hydrogenation to haloaniline but avoiding the occurrence of dehalogenation requires a precise design of highly selective catalysts [14–20]. It is essential to get a deep understanding of the possible reaction mechanisms to enable us to achieve the selective catalysis.

In the recent years, density functional theory (DFT) calculations have been widely employed to understand the surface catalytic reactions at the atomic and molecular levels. To model the mechanism of nitrobenzene reduction, there are two significant problems to overcome. The first challenge is associated with the large size of nitrobenzene molecule, because a larger molecule would considerably increase the number of possible adsorption configurations [21–32], therefore, a significantly more adsorption configurations should be carefully tested in the calculations of nitrobenzene, in contrast to the much fewer adsorption configurations of other smaller organic molecules such as formic acid or methanol. In addition, an increase in adsorption configurations would also lead to an increase in the numbers of possible transition states, which again makes the calculations more complicated and time-consuming [21,22]. The second challenge is associated with the fact that, in the case of weak overlap of electrons/orbitals between the phenyl group and the metal surface, the van der Waals (vdW) interaction is frequently the only force that brings and binds the molecule to the surface [23–25]; the influences of vdW interaction on the large aromatic compounds concerning adsorption, energetics or kinetics, are still less well documented in heterogeneous catalysis. Only a few pioneering works have been made in the study of these large molecules [21,22,26–32]. Saeys et al. calculated benzene adsorption and hydrogenation to cyclohexane on Pt(1 1 1) [21,22]. Mahata et al. reported the mechanism of nitrobenzene reduction over Ni (1 1 1) via direct or indirect mechanisms [26]. With respect to some other large molecules in heterogeneous catalysis, Lu et al. systematically calculated the hydrogenation of guaiacol over Ru(0 0 0 1) and Pt(1 1 1) surfaces involving the C–O bond dissociation [28,29]. Wang et al. studied the activity and selectivity between hydrogenation and decarbonylation of furan and its derivatives on Pd(1 1 1) [30,31]. These studies have provided some initial insights into the surface chemistry of large molecules in heterogeneous catalysis. Despite of extensive experimental studies, there is still lacking theoretical work to elucidate the mechanism of nitrobenzene reduction over platinum catalysts.

In order to provide a better understanding of the nitrobenzene reduction to aniline over platinum catalyst, we have systematically investigated the mechanism using first principle calculations with the inclusion of vdW interactions, for the first time. The closed-packed flat Pt(1 1 1) surface as the thermodynamically most stable facet was used here as an ideal model catalyst for calculations. This paper is organized as follows. The computational method is described in Section 2. The calculated results, including the adsorption of nitrobenzene and aniline, and the hydrogenation and deoxygenation mechanisms of the nitro group, are shown in Sections 3.1 and 3.2. Then the influence of the adsorption of phenyl group at the transition state on both the kinetic barriers and the selective catalysis is further discussed in Sections 3.3 and 3.4. Finally, the main conclusions are summarized. We anticipate this work would be of benefit for the further study of large aromatic compounds in heterogeneous catalysis, molecular engineering and environmental engineering.

2. Computational methods

All the DFT calculations were implemented with the Perdew-Burke-Ernzerh (PBE) generalized gradient approximation (GGA) exchange-correlation functional using the Vienna Ab-initio Simulation Package (VASP) code [33–39]. The projector-augmented-wave (PAW) pseudopotentials were utilized to describe the core electron interaction. Since the exclusion of the vdW interactions in the strongly adsorbed benzene on metals would lead to a significant reduction in the adsorption energy from PBE, the optB88-vdW method as implemented in the VASP code was utilized to describe vdW interactions [23–25]. The cut-off energy was set to 400 eV which was tested to be accurate enough for energy calculations. The vacuum region layers were built more than 12 Å to ensure the slab interaction was eliminated. A $p(3 \times 3)$ supercell was used with $3 \times 3 \times 1$ Monkhorst-Pack k-point sampling for Brillouin zone. The size of supercell agrees with the experimental observation of the benzene coverage [40,41]. During all the optimization process, the bottom half atoms were fixed in the slab while the top half atoms were relaxed. All the transition states were localized with constrained minimization approach and the convergence of forces was set to 0.05 eV/Å [42–44]. In this work, the adsorption energy was defined as: $E_{ad} = E(ad/\mathrm{Pt}) - E(ad) - E(\mathrm{Pt})$, where $E(ad/\mathrm{Pt})$, $E(ad)$, and $E(\mathrm{Pt})$ are the total energies of the adsorbate binding to Pt(1 1 1) surface, free adsorbate in gas phase and clean Pt(1 1 1), respectively.

3. Results and discussions

3.1. Nitrobenzene and aniline adsorption

Experimentally, over a range of catalysts studied, only nitro-group of nitrobenzene was reduced to amino group whilst the phenyl group held, therefore we concentrated on the reduction mechanism of nitro-group in this theoretical study [1–13]. In the surface catalytic reactions, the first stage was the adsorption of nitrobenzene on the Pt(1 1 1) surface. It is worth emphasising that both the phenyl- and nitro-groups are reactive towards binding to Pt surface free sites, and thus the considerations of the adsorption via the phenyl- and nitro-groups are necessary. Firstly, we calculated the adsorption of nitrobenzene via the phenyl group, specifically the center of the phenyl group was located at the top, bridge and hollow sites, respectively, on Pt(1 1 1) surface as the initial structures and then the geometry optimizations were performed.

When phenyl group was located at the Pt top site, nitrobenzene spontaneously desorbed during the optimization since no chemical bonds were formed between the nitrobenzene and Pt(1 1 1) surface. It was found that nitrobenzene stayed parallel above the surface with a height of ~3.5 Å as shown in Fig. 1a. Despite of the relative long distance between nitrobenzene and the surface, the adsorption energy calculated is −1.06 eV, indicating the interaction between nitrobenzene and the Pt surface is actually considerably strong. We conclude that the vdW interaction might make the vital contribution here though the weak overlap of electrons/orbitals between the phenyl group and Pt(1 1 1) surface could also exist. If without consideration of vdW interaction in the calculation, the adsorption energy was lowered to a minute value (-0.15 eV), implying that there is no occurrence of nitrobenzene adsorption, in agreement with the parallel configuration.