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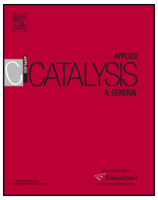

Theoretical analysis of CO + NO reaction mechanism on the single Pd atom embedded in γ-Al_2O_3 (110) surface

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ABSTRACT

The reaction mechanism of CO + NO on Pd/γ-Al_2O_3 (110) has been studied using periodic density functional theory (DFT) calculations in detail. Three pathways to form CO_2, N_2O and N_2 were investigated by the kinetics and the electronic structure of catalyst. The calculated results indicate that the oxygen vacancy O_v plays an important role during the catalytic process, and Pd-O_v pair embedded in γ-Al_2O_3 is proposed to be an active site. The projected density of states (PDOS) analysis indicates that the formation of the oxygen vacancy O_v and the electron transfer between the surface Pd atom and CO or NO molecule are responsible for the catalytic activity of Pd/γ-Al_2O_3 (110).

1. Introduction

The CO + NO catalytic reaction is a major reaction for three-way catalytic converters (NO_x, CO and hydrocarbons) in the automotive exhaust. NO reduction with CO to form CO_2 and N_2 has attracted much attention due to its advantage of simultaneous removal of CO and NO [1–5].

Nitrous oxide (N_2O) is a key intermediate during the reduction of NO by CO, the less ideal pathways are as follows:

$$CO + 2NO \rightarrow CO_2 + N_2O \qquad (1)$$

$$N_2O + CO \rightarrow N_2 + CO_2 \qquad (2)$$

The desired reaction pathway is as follows:

$$2CO + 2NO \rightarrow N_2 + 2CO_2 \qquad (3)$$

The CO + NO catalytic reactions have been investigated previously on Pd/Al_2O_3 [6], Pt-MoO_3/γ-Al_2O_3 [7], Pt-K/Al_2O_3, Pt-Ba/Al_2O_3 [8] and Rh/SiO_2 [9,10] catalysts. Almusaiteer et al. investigated the dynamic behavior of NO—CO reaction on Pd/Al_2O_3 by in situ infrared (IR) spectroscopy combined with TPR and pulse reaction techniques [6]. Da Silva et al. found that the higher N_2 selectivity on Pt-MoO_3/γ-Al_2O_3 is due to the existence of Mo (Mo $\geq$ 8%) [7]. The NCO intermediate plays a major role during the reaction of CO + NO on Pt-K/Al_2O_3 and Pt-Ba/Al_2O_3 [8]. These results have shown that the formation of isocyanate (–NCO) bands around 2240 and 2265 cm^{-1} on the surface of catalysts, respectively.

The kinetics of the CO + NO reaction to form CO_2 and N_2O on Co^{2+}-ensemble/γ-Al_2O_3 catalyst was conceived to be Eley-Rideal mechanism [11]. Ding and co-workers found from a first-principles study that $N_2O_2{}^*$ is the key intermediate to form N_2 on Pd/CeO_2(111) and the formation of the Pd-O_v (oxygen vacancy) is responsible for the catalytic activity [12]. Theoretical studies of the adsorption behavior of the intermediates on the catalytic surface (Ag/Al_2O_3, Cu/Al_2O_3, Ag-Pd/Al_2O_3, etc.) by DFT were performed in our previous research work [13–16].

Although the previous researches provide important insight on the reaction mechanism of CO + NO catalytic reaction, key information regarding the possible intermediates and transition states is still missing. The mechanism of CO + NO catalytic reaction on the supported Pd remains elusive.

In this paper, we discussed on the mechanism of CO + NO catalytic reaction on the (110) surface of Pd-ensemble/γ-Al_2O_3 catalyst by first-principles density functional theoretical (DFT) calculation in detail. Some kinetic models were established to interpret the effects of various factors including the activity sites and the adsorption sites of CO and NO. The results will provide an insight into explore the catalytic mechanism and develop a novel technology for the CO + NO catalytic reaction on the surface of catalysts.

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Table 1
Structure parameters (in Å) calculated by the different DFT functionals in this work compared with the experimental results for γ-Al_2O_3.

	GGA			LDA	Exp.[a]
	PBE	RPBE	PW91	CA-PZ	
Lattice parameters (a = b)	4.816	4.822	4.813	4.700	4.761
Relative deviation(%)	1.155	1.281	1.092	−1.281	
c	13.145	13.186	13.135	12.812	12.994
Relative deviation	1.162	1.477	1.085	−1.400	
$\alpha = \beta$	90	90	90	90	90
γ	120	120	120	120	120
Al—O	1.876	1.879	1.874	1.831	1.855
Relative deviation	1.132	1.293	1.024	−1.293	
Al—O	1.997	2.000	1.996	1.946	1.972
Relative deviation	1.267	1.419	1.217	−1.318	

[a] Experimental values are from Ref. [23–25].

2. Computational method and model

We performed DFT calculations using CASTEP module implemented in the Material Studio (MS) v8.0 environment [17]. GGA/PW91 functional is used to the exchange correlation energy [18]. A slab model of γ-Al_2O_3 (110) surface consisting of 5 atomic layers with a 4 × 4 surface supercell was built in this work. This computational model contains 184 atoms and has a vacuum gap of 15 Å. The ultra-fine quality were carried out in all the calculations. Ultrasoft [19] pseudopotentials (USP) has been used with the 400 eV cutoff energy for the plane-wave basis set. On the basis of the convergence test for k-point grid, the k-point set of 6 × 6 × 6 has been selected for γ-Al_2O_3(110) and Pd/γ-Al_2O_3(110) calculations. The ultra-fine quality is used for geometry optimization, including the energy of 5.0×10^{-7} eV/atom, maximum force of 0.01 eV/Å, maximum stress of 0.02 GPa, and 5.0×10^{-4} Å, respectively. The convergence criteria for SCF calculations was 5.0×10^{-7} eV/atom.

The transition states (TS) were searched using complete linear synchronous transit (LST) and quadratic synchronous transit (QST) method. The searched TS structure were finally subjected to full TS optimizations. All calculated energies included the zero-point vibrational energy (ZPVE).

The single Pd atom embedded in γ-Al_2O_3 (110) surface was fund to have a great influence on the formation energy of the oxygen vacancy (O_v) on the catalyst surface. Moreover, the catalytic activity and versatility of Pd-embedded γ-Al_2O_3 (110) depend on the formation of O_v and the dopant-oxide pairs. For doped Al_2O_3 surfaces, DFT calculations on Ni-doped $(Al_2O_3)n$ (n = 9, 10) [20], C-doped α-Al_2O_3 [21], and La-doped α-Al_2O_3 [22] have also been reported. Therefore, we built the calculated models of a single Pd atom embedded in γ-Al_2O_3 (110) surface.

3. Results and discussion

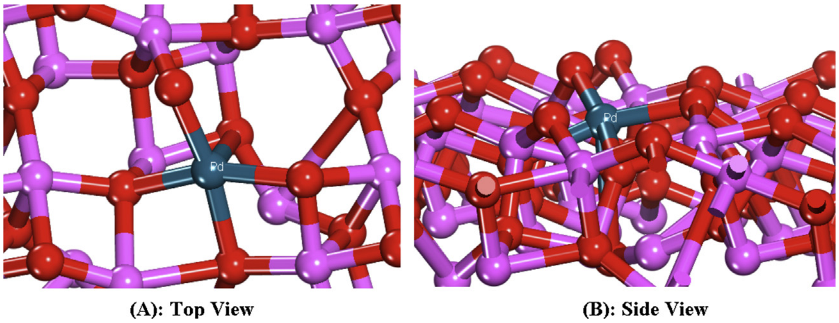
3.1. γ-Al_2O_3(110) and Pd/γ-Al_2O_3(110) surfaces

The calculated structure parameters of γ-Al_2O_3 using GGA/PBE, GGA/RPBE, GGA/PW91 and LDA/CA-PZ functionals are listed in Table 1, respectively. In order to study the performance and limits of different DFT functionals in predicting the structure parameters for γ-Al_2O_3, the relative deviations between the theoretical and experimental values are also listed in Table 1.

The lattice parameters of γ-Al_2O_3 are obtained from in which a = b = 4.761 Å, c = 12.994 Å, $\alpha = \beta = \gamma = 90^\circ$, $\gamma = 120^\circ$ with the atoms locating at Al (0, 0, 0.3521) and O (0.303626, 0, 0.250). The calculated lattice parameters of a and b for γ-Al_2O_3 using GGA/PBE, GGA/RPBE, GGA/PW91 and LDA/CA-PZ functionals are 4.816, 4.822, 4.813, 4.700 Å, respectively. In comparison with the same experimental value of 4.761 Å, the relative deviations between the calculated structure parameters and experimental values are about 1.155% for GGA/PBE, 1.281% for GGA/RPBE, 1.092% for GGA/PW91 and −1.281% for LDA/CA-PZ. The calculated lattice parameters of a, b and c for γ-Al_2O_3 using GGA/PW91 functional show good agreement with experimental value [23–25].

There are two types of Al-O bonds (Al: IV, V) on the surface of γ-Al_2O_3, each surface Al atom coordinates with four or five oxygen atoms. The optimized two Al—O bond lengths by GGA/PW91 are 1.874 and 1.996 Å, respectively, which also agrees well with the experimental values of 1.855 and 1.972 Å [23–25].

In this work, we use γ-Al_2O_3(110) as the support because (110) termination is the most abundant exposed surface of γ-Al_2O_3 [26–28]. For the optimized Pd/γ-Al_2O_3(110) (Fig. 1), the corresponding bond lengths of the surface O adjacent to Pd atom are 2.003, 2.093, 2.076 and 2.120 Å, respectively, which are longer than



(A): Top View (B): Side View

Fig. 1. Schematic structure models for Pd/γ-Al_2O_3 (110), in which the single Pd atom substitutes the surface Al atom: (A) top view; (B) side view. Red, dark cyan and magenta spheres represent O, Pd and Al atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)