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DFT insight on oxygen adsorbed platinum trimer cluster (Pt_3) for CO oxidation

Satyajit Dey Baruah, Nand K. Gour, Plaban J. Sarma, Ramesh C. Deka *

Department of Chemical Sciences, Tezpur University Tezpur, Napaam, Assam 784 028, India

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ABSTRACT

Oxidation of CO has been performed systematically over oxygen adsorbed platinum trimer cluster (Pt_3) using hybrid density functional theory (DFT) method. Terminal, end on and bridging site of oxygen adsorbed Pt_3 have been employed for the oxidation reaction. We have characterized all the stationary points on the potential energy surface along with transition states for prediction of most suitable CO oxidation pathway. The binding energies are determined for predicting stability of adsorbed oxygen and carbonmonoxide over platinum trimer. Evaluated barrier height calculations on end on oxygen adsorbed platinum cluster have shown minimum activation energy indicating Pt_3O to have the potentially better catalytic activity for CO oxidation.

1. Introduction

Carbon monoxide (CO) is a deadly, odorless, colorless and poisonous gas. Extensive rise of CO in the environment have stemmed from the incomplete burning of fuels such as coal, wood, kerosene oil and other petroleum products. It is acknowledged as a weak greenhouse gas but it seems to exhibit an indirect effect on the climate of the Earth. Its existence in the atmosphere has markedly contributed towards the ineludible growth of the harmful greenhouse gases. It greatly differs from most other pollutants in its inherent capability to survive in the atmosphere to undergo reactions with hydroxyl radical. This is in turn has led to the steep rise in the concentration of methane [1]. One of the severe consequences of increased concentrations of CO is carbon monoxide poisoning, which is fatal to the human health and in most cases it may lead to death. This has provoked a deep scientific interest in the removal of this harmful gas in recent years. Due to the poisonous nature of CO present in car exhausts and in the fuel cell catalyst removal of CO has gained utmost importance in the field of industrial research [2,3]. Consequently, CO oxidation has turned to be one of the most studied reactions in catalytic chemistry. One of them is conversion of CO into CO_2 in presence of molecular oxygen. Even though, CO_2 is also a greenhouse gas but it is less harmful in comparison to CO. The oxidation reaction is,

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

Several catalysts were developed in late twentieth century for the oxidation of carbon monoxide based on precious metals like gold, palladium, rhodium and platinum. Haruta and their coworkers [4] made a significant breakthrough in 1987 in their work that effectively displayed the high catalytic activity of gold nanoclusters (less than 10 nm) dispersed on transition metal oxides for low temperature CO oxidation. This has led to the extensive research on metal nanoparticles catalyzed oxidation of CO. But catalytic activities of these catalysts have seen to be dependent on the size and shape of the metal nanocluster. Theoretical studies were performed by Norskov et al. [5] on gold nanomaterials modeling flat and stepped surfaces providing an explanation for its immense reactivity. In addition to that, this group went on working on adsorption of molecules and oxidation of CO on gold clusters [6]. Platinum clusters Pt_n (8–10) were shown to exhibit catalytic oxidative dehydrogenation reaction of propane more effectively compared to the bulk platinum and vanadium catalyst [7]. Catalytic activities of various single-metal atoms (Pt, Rh, Pd, Au, Co, Cu, Ru, and Ti) supported by the iron-oxide surface, using DFT computations were also explored [8,9]. Experimentally, sound progress was made on various substrates such as graphene, shape selective zeolites and open metal oxide supports [10–18] of single metal atoms. Theoretical research has also reflected the high catalytic activity of CO oxidation on single metal atom embedded on grapheme [19–23] or graphene oxide [24] or BN nanosheet [25,26] or iron oxide [27].

* Corresponding author.
E-mail address: ramesh@tezu.ernet.in (R.C. Deka).

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CO oxidation on platinum (1 1 1) surface with the help of molecular beam technique has been studied long back [28] which convincingly increased the work on platinum surface for CO oxidation as to be seen in the recent years [29]. Significant work has also been reported over small palladium and gold clusters in this early decade where the oxidation of carbon monoxide is performed over palladium trimer and gold trimer [30]. Extensive research has been realized on cluster because of their unique and

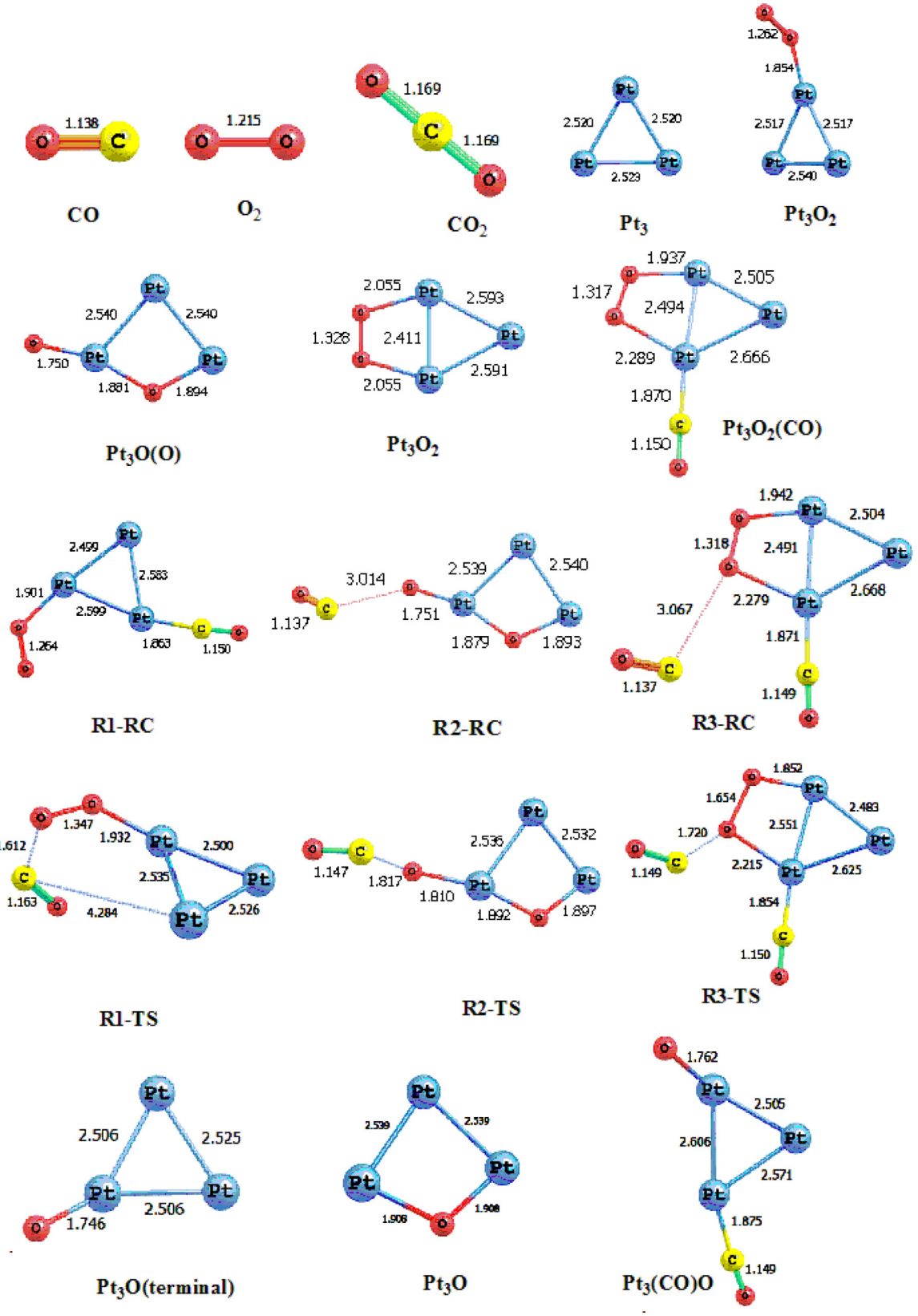

Fig. 1. Optimized geometry of the all species at B3LYP/6-31 G(d,p)/Lanl2DZ level of theory.