Journal of CO_2 Utilization 16 (2016) 257–263

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Interaction of CO_2 with metal cluster-functionalized ionic liquids

Changqing Dai, Yang Yang, Adrian Fisher, Zhiping Liu*, Daojian Cheng*

International Research Center for Soft Matter, State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China, People's Republic of China

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form 11 July 2016
Accepted 13 August 2016
Available online xxx

Keywords:
CO_2 conversion
Metal cluster
Ionic liquids
Density functional theory calculations

ABSTRACT

Metal cluster-functionalized ionic liquids (ILs) exhibit promising characteristics for CO_2 conversion, however, progress in this area is currently limited due to the lack of understanding of the underlying reaction mechanisms involved. In this article the interaction of CO_2 with metal cluster-functionalized ILs is studied and provides key insights into the initial stages of CO_2 activation and subsequent conversion. The interaction of CO_2 with Au-Pd cluster-functionalized ILs is investigated using density functional theory (DFT) calculations based on the DFT-B3LYP approach and the mixed basis sets of 6-31+G (d, p) and LANL2DZ. It is found that single Au or Pd atoms can interact with ILs and results in a significantly stronger interaction of Au with ILs than that of Pd. More broadly it is also found that Au-Pd cluster-functionalized ILs can significantly enhance the interaction of CO_2 with ILs. Interestingly the interaction of CO_2 with Au-Pd cluster-functionalized IL is found to be highly dependent on the size and composition of the cluster. Among the systems studied, Au_1Pd_2-functionalized IL yields the strongest interaction with CO_2. Our results highlight a non-monotonous behavior for the composition- and size-dependent interaction of CO_2 with Au-Pd cluster-functionalized ILs. It is proposed that these findings can provide a new roadmap for the design and development of metal cluster-functionalized ILs for CO_2 conversion applications.

1. Introduction

Despite recent advances in renewable energy technologies fossil fuels still provide roughly eighty percent of the energy demand required to support society. The resulting increase in atmospheric CO_2 concentration has been strongly implicated as a key driver in global warming [1–5]. Recently, various methods of carbon capture and sequestration (CCS) have been proposed to reduce CO_2 emissions [6–8]. Ionic liquids (ILs), as potential capture agents, show many unique properties, such as negligible vapor pressure, a broad range of liquid temperatures, high thermal stability, good CO_2 solubility and tunable physicochemical characteristics [9–11]. More interestingly, imidazolium-based ILs [12] could be used to chemically capture CO_2 in combination with amines to form a liquid carboxylate salt. This new strategy has been proposed to help overcome the limitation of low solubility from physical adsorption.

More recently, the capture, utilization, and storage of CO_2 (CCUS) has received increasing attention due to the potential for the use of CO_2 as a raw material. This harmless C1 source has been shown to be able to produce many useful chemicals, such as carbon monoxide (CO), methane (CH_4), methanol (CH_3OH), formic acid (HCOOH) and formaldehyde (HCHO) [3,5,13–20]. However, major challenges for recycling CO_2 exist including; the high cost of collecting CO_2 from atmosphere, as well as the low activity and selectivity of the catalysts. The catalytic aspects can be addressed by the use of metal nanocatalysts [13,19,21–23] and it has been found that monodisperse Au nanoparticles can improve the selectivity of catalytic reduction of CO_2 to CO, due to the optimization of the available binding sites of the reaction intermediates [24]. In addition, Pd clusters deposited on TiO_2 encourage the formation of CH_4 rather than CO in the conversion of CO_2 [25]. Thus, Au-Pd bimetallic clusters have been identified as promising catalysts for the conversion of CO_2.

Combining the benefits of metal cluster and ILs, metal cluster-functionalized ILs offer exciting opportunities for tunable and efficient catalyst for CCUS. However, the interaction of CO_2 with metal cluster-functionalized ILs is still essentially uncharacterized. These current limitations can be addressed by the application of high performance computer, theoretical methods, such as density functional theory (DFT) [26–30], which have proved to be valuable tools to study the interaction of CO_2 with metal cluster-functionalized ILs. In previous work, DFT calculations have been used to study the interactions of metal clusters with ILs [31], as

* Corresponding authors.
E-mail addresses: liuzhp@mail.buct.edu.cn (Z. Liu), chengdj@mail.buct.edu.cn (D. Cheng).

http://dx.doi.org/10.1016/j.jcou.2016.08.004

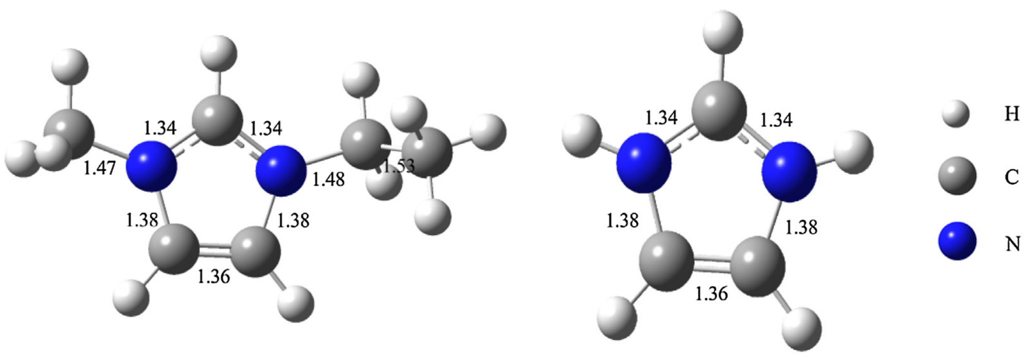

Fig. 1. The equilibrium geometry of 1-ethyl-3-methylimidazolium cation ($EMIM^+$ on the left) and 1,3-dihydro-imidazolium cation ($HHIM^+$ on the right).

well as the interactions of CO_2 with ILs [32]. However, to the best of our knowledge, no studies on the interaction of CO_2 with metal cluster-functionalized ILs have been reported.

In this work, the interaction of CO_2 with Au-Pd cluster-functionalized ILs is investigated by DFT calculations based on the DFT-B3LYP approach using the mixed basis sets of 6-31+G (d, p) and LANL2DZ. The investigations reported have focused on the size and composition dependent interactions of CO_2 and Au-Pd cluster-functionalized ILs.

2. Method of calculations

Density functional theory (DFT) has been shown to be a powerful and effective computational tool to investigate electron correlation effects especially for organometallic compounds [33,34]. For the investigations presented in this article imidazolium-based ILs with either 1-ethyl-3-methylimidazolium ($EMIM^+$) or 1,3-dihydro-imidazolium cations ($HHIM^+$) are used and then functionalized with Au-Pd clusters. It has been shown previously that metal systems, such as nanoparticles or clusters can be functionalized and stabilized with ionic liquids, while not adversely affecting the properties of the ILs [35].

Fig. 1 shows the equilibrium structures of $EMIM^+$ and $HHIM^+$, obtained by DFT calculations. It is interesting to note that the replacement of the functional groups, methyl and ethyl has little influence on the structure of the imidazolium rings.

The geometries of Au-Pd cluster-functionalized imidazolium ILs and CO_2 were fully optimized by using DFT calculations with the B3LYP functional, which has been successfully employed to study ILs. It is noted that dispersion-corrected DFT method can improve the accuracy of DFT calculations in modeling the ILs [36,37]. The 6-31+G (d, p) basis set was used for imidazolium cations and CO_2, and Lanl2DZ basis sets were applied for Au-Pd clusters [38]. In the case of the CO_2 absorbate it has been shown to accept a single electron to form CO_2^-, in IL environments. Accordingly, CO_2^- can directly react with the ILs to form a complex [39,40].

The harmonic vibrational frequencies and total energies were calculated for all the optimized geometries. No imaginary frequencies were found in all the stable structures. The total energy was corrected by the zero-point energies (ZPEs) and real frequencies were obtained. The analysis of electronic and orbital properties of stable structures were accomplished with the Multiwfn code [41] and the natural bond orbital (NBO) method in the Gaussian 09 code package [42].

The interaction energy (ΔE) of Au (or Pd) atom with ILs was calculated by

$$\Delta E = E_{AB} - E_A - E_B \quad (1)$$

where E_{AB} is the total energy of the system of the metal atom-functionalized IL, and E_A and E_B are the energies of the metal atom and IL respectively.

The interaction energy (ΔE) of CO_2 with metal cluster-functionalized ILs at different sites was calculated by

$$\Delta E = E_{system+CO_2} - E_{system} - E_{CO_2} \quad (2)$$

where $E_{system+CO_2}$ is the total energy of the system including the CO_2 interaction with metal cluster-functionalized IL, E_{system} is the energy of the system of metal cluster-functionalized IL, and E_{CO_2} is the energy of an isolated CO_2 in vacuum.

3. Results and discussion

3.1. Interaction of metal atoms with ILs

The metal atom-functionalized ILs were constructed by using single Au or Pd atoms to replace the H atom in the imidazolium ring at different positions. Fig. 2 shows the configuration and the

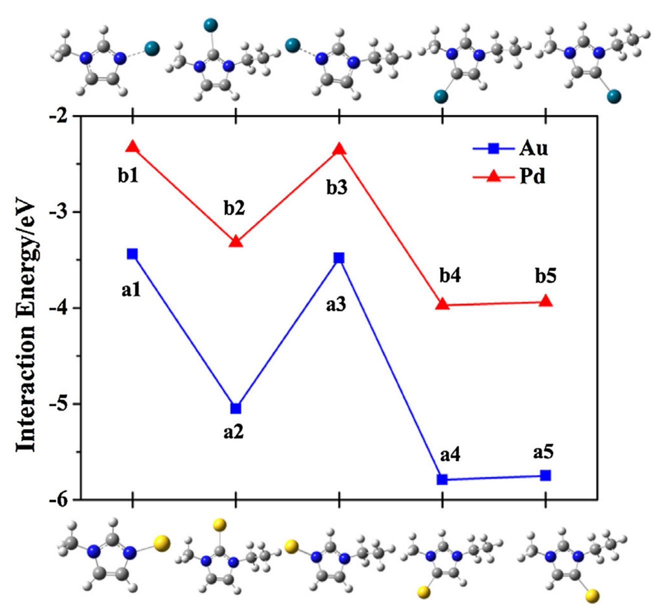

Fig. 2. The configuration and the corresponding interaction energy of single Au or Pd atom interacted with $EMIM^+$ at different positions (a1-a5 for Au, b1-b5 for Pd). The yellow ball stands for Au atom and the cyan ball stands for Pd atom (same in the following figures). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)