



Molecular steps for the syngas conversion on the Rh₆ cluster

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ABSTRACT

In the present computational study, we investigate the competitive reaction pathways for the conversion of syngas to the formation of C₁ and C₂ oxygenated compounds such as formaldehyde, methanol, acetic acid, acetaldehyde and ethanol on a Rh₆ cluster. Moreover we also present pathways for the formation of methane and water, which are considered to be the major by-products in the syngas conversion. Our results demonstrate that the formation of the C₁ oxygenates takes place via the hydrogenation of the adsorbed CO molecule while the formation of C₂ oxygenates proceeds in two steps, i.e. CO dissociation to produce CH_x species followed by CO and/or HCO insertion.

An analysis obtained from the present calculations reveals that the product formation on Rh₆ cluster depends upon the CO:H₂ coverage. Under hydrogen rich conditions, the products will mainly consist of CH₃OH, CH₄ and water. The kinetic analysis based on rate constants obtained from harmonic transition state theory indicates that the initial step of CO hydrogenation is the rate-limiting step. Moreover, results suggest that the CO dissociation and the insertion steps for the formation of C₂ oxygenates on Rh₆ cluster have lower barriers compared to that on the Rh(1 1 1) surface.

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1. Introduction

Fischer–Tropsch (F–T) mechanism provides an alternative route to produce liquid fuels via the catalytic conversion of syngas (CO + H₂) derived from natural gas, coal or biomass into olefins or paraffins and oxygenated compounds such as alcohols, ketones, aldehydes, acids, esters, etc. [1,2]. Although methane and water are the main by-products in the syngas conversion, the selectivity towards other compounds such as alkanes, alkenes and oxygenated compounds needs to be high [1–3]. Transition metals such as Ru, Co and Fe are suitable catalysts for the synthesis of long chain hydrocarbons such as paraffins or olefins [2–6]. On the other hand, Rh-based catalysts are better candidates for the formation of oxygenates such as alcohols, aldehydes and for the methanation reaction [7]. Among the oxygenated compounds, ethanol is considered as a promising alternative for fuel [3,8,9]. Studies have shown that the supported Rh-catalysts are highly selective for the formation of alcohols and aldehydes [10–13]. Recently, in a pioneering work Pan et al. have shown that the Rh–Mn nanoparticles confined inside carbon nanotube increase the overall formation of ethanol [14].

A low yield for the formation of ethanol is due to the molecular mechanism which involves the CO dissociation to create the CH_x species and the insertion of the undissociated CO molecule

in the CH_x species [3,15–17]. Hence, for a selective ethanol formation, it is necessary to find an optimum path which will create the CH_x species followed by the CO insertion. In the past, several mechanisms have been conjectured for the synthesis of C₁ and C₂ oxygenated compounds. Sachtler and Ichikawa have experimentally shown that CO insertion into surface–alkyl bonds creates acyl species, leading to oxygenates such as alcohols or aldehydes [15]. These studies have been carried out on SiO₂-supported Rh-catalysts in presence of promoters such as manganese or alkali ions. Choi and Liu have investigated the reaction path for the formation of ethanol on Rh(1 1 1) surface [18]. They proposed that the rate-limiting step in this process is to create the CH_x species followed by the CO insertion in the CH₃ species [18]. Recent experimental and theoretical studies have suggested that the yield towards oxygenated compounds can be increased by using promoters such as Mn [17]. The selectivity of the products produced on Rh clusters has also been controlled by the use of zeolites as a support. Rao et al., have shown that the encapsulated Rh clusters in zeolite Y act as active sites for the conversion of syngas to alcohols and hydrocarbons [19]. Gates et al. have extensively studied the role of carbonylated as well as decarbonylated Rh₆ clusters supported in NaY-zeolite in syngas conversion [12,20]. Their studies suggested that the zeolite plays a unique role in entrapping the Rh clusters and in increasing their selectivity.

Considering the significant role of Rh clusters in the formation of oxygenated compounds, mainly ethanol from the syngas, a detailed potential energy surface of syngas conversion on Rh₆

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cluster has been investigated. The competitive reaction pathways for various oxygenates formation and as well the paths for the formation of methane and water as by-products has been established. The manuscript deals with the following issues in the syngas conversion on Rh₆ cluster: (1) what are the competitive reaction pathways? (2) what is the rate-limiting step on small Rh clusters? (3) what are the intermediates which lead to the C₁ and C₂ oxygenated products? (4) how does the reaction pathway on Rh₆ cluster differs from that on the Rh surface?

2. Computational details

The calculations have been performed using a density functional approach with plane wave basis set in conjunction with projected augmented wave-functions (PAW) as implemented in the VASP code [21,22]. Spin polarized calculations were done using the generalized gradient approximation (GGA) with the PBE functional for the exchange correlation. All calculations have been carried out with clusters being placed in a cubic supercell maintaining a vacuum of 10 Å between the neighboring images. The calculations were restricted to the gamma point in the Brillouin zone sampling. The energy cut-off used for the plane wave was 400 eV. The energy was converged until the forces on the atoms were less than 0.05 eV/Å and the difference in energies between subsequent steps is less than 10⁻⁴ eV. The structures were optimized using the conjugate gradient technique. The reaction paths for the formation of C₁ and C₂ species and the diffusion of reaction intermediates have been generated by the nudged elastic band (NEB) as implemented in VASP [23]. In all pathways, twelve images have been generated between the initial and the final states using the interpolation method. Optimization of these images have been carried out using the steepest descent method. Transition states were characterized by the presence of only one imaginary frequency and rate constants were computed using the conventional harmonic oscillator transition state theory approximation [24]. Energies are reported after appropriate zero point energy corrections.

3. Results and discussions

This section is organized as follows: it begins with a discussion on the adsorption of C₁ and C₂ oxygenates studied in the present work, followed by a discussion on adsorption energies of CO in the presence of coadsorbed H and CO species. Subsequently, the results of CO hydrogenation and the formation of C₁ and C₂ oxygenated compounds have been summarized.

3.1. Adsorption of C₁ and C₂ oxygenates on Rh₆ cluster

The structures and adsorption energies of C₁ and C₂ oxygenates along with the CH₄ and H₂O molecules on the Rh₆ cluster are presented in Table 1. One can see that the CH₂O is strongly adsorbed relative to CH₃OH on the Rh₆ cluster implying that CH₂O can be a potential intermediate en route to other oxygenated compounds. In the case of C₂ oxygenates, the CH₃CHO is more strongly adsorbed in comparison to other C₂ oxygenates (Table 1). The stability of aldehydes on the Rh₆ cluster can be attributed to the π–σ-bond formed between the π of the C–O bond of aldehydes and σ of the Rh–Rh bond. The strong adsorption of aldehydes however indicate that they will be difficult to desorb compared to other oxygenates and hence are less likely to be the final product of syngas conversion on Rh₆ clusters.

The reader should refer to the supplementary information for a discussion on structural properties of the Rh₆ cluster and CO adsorption. In addition, efforts were also made to understand the effect of coadsorbed CO or H on the adsorption behaviour of CO

Table 1

Structures and the adsorption energies of C₁, C₂ oxygenated compounds, CH₄ and H₂O on Rh₆ cluster. Grey, yellow, red and blue spheres correspond to Rh, C, O and H atoms, respectively.

Adsorbed molecules	Structures	Adsorption energies (kJ/mol)
CH ₂ O		-157
CH ₃ OH		-47
CH ₃ CHO		-129
CH ₃ COOH		-59
CH ₃ CH ₂ OH		-51
CH ₄		-24
H ₂ O		-35

by investigating the structure and energetics of Rh₆(CO)_n (n = 1–3) and Rh₆(CO)_n(2H) (n = 1–3), Rh₆(CO)_n(4H) (n = 1, 2). Dissociatively adsorbed hydrogen atoms prefer a hollow or bridge site and never compete for the top-site on Rh₆ cluster. Results of CO adsorption energies are compiled in Table 2. As can be seen from Table 2, adsorption energies of CO are not influenced very strongly by the coadsorbed species. A top-site CO adsorption is always favored over a hollow site, and the adsorption energy of a top-site CO is ~210 kJ/mol.

3.2. Reaction pathways for the formation of C₁ oxygenates, CH_x intermediates and water

Scheme 1 (Fig. 1) represents the formation of CH_x (x = 0, 1, 2) intermediates, CH₂O and H₂O from the CO and 2H coadsorbed on the Rh₆ cluster, investigated in the present study.

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