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Mechanistic insight into the quantitative synthesis of acetic acid by direct conversion of CH_4 and CO_2: An experimental and theoretical approach

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ABSTRACT

Conversion of CH_4 and CO_2 into value-added products has vital environmental and economic importance. Their direct conversion to acetic acid is challenging due to their high activation energy. Hence, kinetic and mechanistic information are crucial for the carbonylation of CH_4 with CO_2. Regarding this, single and dual component catalysts with different combinations of ZnO-, CeO_2-, and MnO_2- supported montmorillonite (MMT) were prepared and characterized by XPS, Raman, and XRD. Quick solid-state NMR, TGA, and FT-IR techniques were used and Langmuir-Hinshelwood model was considered to investigate mechanistic steps involved in the conversion of CH_4 and CO_2 to acetic acid. The obtained mechanistic and kinetic results were also theoretically proved by density functional theory (DFT) calculations. We found that ZnO and CeO_2 dual active sites preferentially adsorb the CH_4 and CO_2, respectively that avoid surface adsorption competition. The rate of acetic acid formation was maximum when these sites exist at appropriate concentration (Ce: 0.44 wt%, Zn: 2.20 wt%). DFT calculations elucidated that the formation of acetic acid is strongly favored on ZnO catalyst with easier migration of the adsorbed CO_2 from CeO_2 to the ZnO side.

1. Introduction

Research on converting abundant, unwanted, and global warming gases to value-added products has been attracting great attention as a critical challenge for mitigating climate change on earth. It is in the interest of science to develop solutions that maintain and promote a "green" earth. Many preliminary precautions, such as reducing coal burning, planting trees, have been taken to minimize pollution and global warming. However, in populous developing countries, such as China and India, coal utilization is still necessary to meet large energy demand. Therefore, steps must be taken to utilize byproducts from all types of polluting activities. To that end, the consumption of CH_4 and CO_2 seems a potential solution associated with climate change[1–8]. Activation and utilization of CH_4 have been widely studied [9–12]. However, research on its conversion to oxygenates, such as methanol, acetic acid, and formaldehyde, is limited due to the high bond energies of CH_4 ($\Delta H_{C\text{-}H} = 439.57\ \mathrm{kJ\,mol^{-1}}$) and the lack of knowledge concerning catalyst properties and kinetic parameters involved in product formation mechanisms. Among oxygenates of CH_4, the preparation of acetic acid is much difficult as it requires three different reaction steps as shown below:

$$\text{Step 1: } CH_4 + H_2O \rightarrow CO + 3H_2,\ \Delta H^{o} = 206\ \mathrm{kJ/mol} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2,\ \Delta H^{o} = -41\ \mathrm{kJ/mol} \tag{2}$$

$$\text{Step 2: } CO + 2H_2 \rightarrow CH_3OH,\ \Delta H^{o} = -102\ \mathrm{kJ/mol} \tag{3}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O,\ \Delta H^{o} = -131\ \mathrm{kJ/mol} \tag{4}$$

$$\text{Step 3: } CH_3OH + CO \rightarrow CH_3COOH,\ \Delta H^{o} = -241\ \mathrm{kJ/mol} \tag{5}$$

Each step reaction needs different types of catalysts and high temperature. Hence, the current focus is on forming acetic acid in a single step by direct conversion of CH_4 using a carbonylating agent such as CO or CO_2.

A perceptible work on the synthesis of acetic acid by carbonylating CH_4 in a single step has been achieved by utilizing noble metals [13–15] such as Pd [16] and Rh [17] catalysts. Few combined experimental and theoretical studies [18–21] have been performed in order to understand mechanism and kinetics of this reaction, as listed in Table 1. In the last decade, those noble metals have been replaced by 3*d* transition metals such as Cu [22] and Zn [23]. Both the active metals (Cu and Zn) are Lewis acids and CH_4 is capable to fragment over acidic

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Table 1
Literature survey on various catalysis for acetic acid production.

Year	Catalyst	Carbonylating agent	Reaction system	Yield/Remark	Reference
2003	$RhCl_3$	CO	Homogeneous	Expensive catalyst, Lower selectivity, needs promotor, complicated system	[18]
2006	Pd^{2+}	CO	Homogeneous	Expensive catalyst, Harsh reaction medium, complicated mechanism, No cyclic reaction	[19]
2007	Amavadine related vanadium complexes	CO	Homogeneous	Harsh reaction medium, complicated mechanism,	[21]
2012	Au(I)-ZSM-5	CO_2	Heterogeneous	Expensive catalyst, reactant adsorption competition,	[25]
2014	Rh	Syngas	Heterogeneous	Poor selectivity, Expensive catalyst, complicated mechanism	[20]
2017	$ZnO-CeO_2/MMT$	CO_2	Heterogeneous	Easy system, cheap catalyst, cyclic mechanism, no reactant adsorption competition	This work

catalysts [15]. They also demonstrate an affinity for CO_2, forming surface carbonates. However, CO_2 is an acid itself. Hence, the concept of CO_2 adsorption on another acidic active metal site is unexpected and not easy to explain. Moreover in these cases, there exists a surface adsorption competition between two reactant gases CH_4 & CO_2. Such phenomena may slower the kinetic parameters of acetic acid formation reaction. The stability of intermediate anions over active site, their ionic attraction strength to the active site also contribute to the total transformation of the gases into products. Therefore, the size of active site, which accounts for strength of surface intermediate, would be a crucial parameter for this reaction. All these vital parameters have not been explored and thus there is no information about how to synthesize acetic acid in a quantitatively way.

There are few theoretical studies on the direct conversion of CH_4 and CO_2 to acetic acid [18,19,24,25]. Some researchers [24,25] used metal-exchanged zeolite catalysts, and identified that the active site of surface reaction is the exchanged metal atom. In addition, they analyzed that either CH_4 activation step [24] or CO_2 insertion step into the metal-CH_3 bond [25] is a possible rate-determining step (RDS). Meanwhile, Zhao et al. [26] investigated the direct conversion of CH_4 and CO_2 by using the Zn-doped ceria catalyst. They elucidated the active site is a doped-Zn atom onto the ceria, which reduces the activation energy for CO_2 insertion step into Zn—CH_3 bond that is the RDS. This is attributed to the destabilization of the Zn—CH_3 bond by low electronegativity of the doped Zn. However, these kinds of catalysts have only a single active site. On the contrary, a catalyst we are suggesting in this study has dual-active site, which is expected to have its unique catalytic behavior.

In this work, to avoid adsorption competition between gases, we prepared dual active-site catalysts containing two different metal oxides supported on montmorillonite (MMT) zeolite. Rabie et al., recently, reported the possibility of quantitative acetic acid formation over a catalyst with dual active sites [27]. As an extended step, we are pinpointing the above explained fundamental properties of catalyst that aid higher selectivity towards acetic acid. For the study, various catalysts (CeO_2-ZnO/ MMT, MnO_2-ZnO/MMT, and CeO_2-MnO_2/MMT) were prepared by varying metal oxide combination to explore the effects of Lewis acidity, atomic size, reactant adsorption, and oxidizing properties. MMT was chosen for improving the dissociation of CH_4 on its oxygen sites as it is reported that CH_4 activation increases over oxygen rich surfaces [28]. Several experiments were performed to explore the importance of those fundamentals and a mechanism was deduced based on experimental outcome. The mechanism and energies of each intermediate steps were further calculated and ensured by density functional theory (DFT) calculations. Energies required for each step in forming acetic acid were calculated for both CeO_2 and ZnO, respectively. Results were well matched and confirmed that the experimentally drawn intermediates which are favorably formed over different active sites possess the lowest energy in DFT calculations as well. Hence, a generalization of factors that favor formation of higher acetic acid is drawn out as conclusions. Despite there are few DFT reports on this reaction over zinc and cerium catalysts [29], to the best of our knowledge, this is the first attempt to study the reaction mechanism for acetic acid synthesis over catalyst having dual active sites.

2. Experimental

2.1. Starting materials

Cerium(III) nitrate hexahydrate (99%, Sigma-Aldrich), Zinc nitrate hexahydrate (98% Sigma-Aldrich), Manganese(II) nitrate tetrahydrate (> 97% Sigma-Aldrich), Montmorillonite K 10 powder (Sigma-Aldrich), Double distilled water, methane gas (99.95% purity), and carbon dioxide gas (99.999% purity) were used as received.

2.2. Catalyst preparation

1 g of montmorillonite zeolite was dispersed into 50 mL of water contained in a beaker. This system was stirred for 48 h with a magnetic bead at rate 600 rpm and was sonicated for 4 h to achieve well dispersion of zeolite nanolayers. To this solution, nitrate solutions of desired active metal with appropriate concentration were added. The particles solution was stirred further for 25 h. In the next step, the mixture was centrifuged, filtered and then washed with distilled water to remove additional ions from the metal surface. The product was dried at 110 °C and ground to fine powder. Finally, calcination was done at a ramping heat rate of 2.5 °C for 4 h 40 min to reach 700 °C in the air medium. The final temperature was further maintained for 1 h. Washings with water was avoided when particular concentration of metal oxide was required on support. Same procedure followed for single oxide supported catalysts keeping total moles of active site equal to that of dual component catalysts.

2.3. DFT calculations

We performed plane wave density functional theory (DFT) calculations by employing the Vienna Ab Initio Simulation Package (VASP) [30–33]. We used the Perdew-Burke-Ernzerhof (PBE) functional based on generalized gradient approximation (GGA) to treat the exchange-correlation energy [34]. To consider dispersion force, a semi-empirical DFT-D3 method proposed by Grimme was applied [35]. In the expansion of the plane wave, a kinetic cutoff energy of 400 eV was employed. The residual minimization method for electronic relaxation was exploited to calculate the total energy, which was accelerated using Methfessel-Paxton Fermi-level smearing [36] with a width of 0.05 eV, and spin polarization was considered in all calculations. Geometry optimization was carried out using a conjugate gradient algorithm until the forces on all unconstrained atoms were less than 0.03 eV/Å. To prevent an artificial electrostatic field, dipole corrections were applied in the surface normal direction to compute all energies reported here [37,38]. The GGA + *U* approach was employed to correctly describe the localized nature of the 4*f* electrons of Ce [39,40]. Here, a Hubbard parameter *U* value of 4.5 eV was selected based on previous studies [41,42]. Meanwhile, according to previous theoretical reports of the