



Quantum mechanical study of CO₂ and CO hydrogenation on Cu(111) surfaces doped with Ga, Mg, and Ti



Yohaselly Santiago-Rodríguez, Erick Barreto-Rodríguez, María C. Curet-Arana*

Department of Chemical Engineering, University of Puerto Rico, Mayaguez Campus, Road 108 km 1.1, Mayaguez 00681-9000, Puerto Rico

ARTICLE INFO

Article history:

Received 2 February 2016
Received in revised form 31 May 2016
Accepted 4 July 2016
Available online 5 July 2016

Keywords:

CO₂/CO hydrogenation
Metal-doped copper surfaces
Density functional theory
Reaction mechanism
Synthesis of methanol formic acid, formaldehyde

ABSTRACT

DFT methods were used to analyze metal (M)-doped Cu(111) surfaces to identify surface alloys that could catalyze the hydrogenation of CO₂. The adsorption of relevant species for CO₂/CO hydrogenation were studied on Cu(111) surfaces doped with Ga, Mg, and Ti. Preferred adsorption sites, geometries, and binding energies for relevant intermediates were determined. A systematic study of the thermochemistry of plausible surface reactions for CO₂/CO hydrogenation on Ga/Cu(111), Mg/Cu(111), and Ti/Cu(111) was performed to postulate reaction mechanisms for the synthesis of formic acid, formaldehyde, and methanol. Our results suggest that Ga/Cu(111) and Mg/Cu(111) surfaces might be promising catalysts for the synthesis of methanol from CO₂ hydrogenation. CO₂ is activated by chemisorption on Mg/Cu(111) and Ti/Cu(111), but the latter surface has a strong interaction with O, which inhibits the last reaction steps and the desorption of the products. Our results demonstrate that the thermochemistry of CO₂ hydrogenation for the synthesis of the different products varies drastically depending on the dopant on Cu(111). Furthermore, our results suggest that the formation energies of HCOO, CH₂O, CH₃O, and HCO are good descriptors for catalyst screening.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Fossil fuels are currently the main carbon source in chemical industry. Because these resources are expected to be depleted and their combustion is the major cause of CO₂ emissions to the atmosphere, the need for finding alternative carbon sources has sparked interest in using renewable sources. The conversion of CO₂ into valuable organic compounds promises to be a potential approach to reduce the environmental impact of CO₂ emissions, and to generate alternate sources of energy and feedstock.

Cu-based catalysts (e.g. copper oxides, supported and composite Cu catalysts) have been extensively employed for the synthesis of methanol [1–5] and carbon monoxide [6,7] through the hydrogenation of CO₂. Methanol is industrially produced from CO, H₂ and small amounts of CO₂ using Cu/ZnO/Al₂O₃ as catalyst at high pressures (50–100 bar) [8]. This catalyst, however, has three limitations: it is susceptible to poisons usually present in syngas sources, it has been observed that the methanol productivity is low in the absence of CO [9] and at low pressures, significant amounts of CO are formed through the reverse water-gas shift (RWGS) reaction

[10]. The RWGS reaction competes with the methanol synthesis from CO₂ hydrogenation. Experimental and theoretical results indicate that the rate of the RWGS reaction is approximately two to three orders of magnitude faster than the methanol synthesis on Cu nanoparticles, resulting in CO accumulation on the catalyst surface [5]. The RWGS reaction is endothermic, while the hydrogenation of CO₂ to methanol is an exothermic reaction, as described in Table 1 [11]. However, the hydrogenation of CO to methanol is even more exothermic than CO₂ hydrogenation [12]. Consequently, in addition to high pressures, relative low temperatures (> 240 °C) are required to favor the hydrogenation of CO₂ to methanol. High reaction temperatures (e.g. 500–873 K) typically favor the formation of undesired products, such as CO, hydrocarbons, and higher alcohols [4].

In an effort to find efficient catalysts for the hydrogenation of CO₂, different metal dopants or promoters have been previously studied to modify the conventional catalyst used for CO₂ hydrogenation and improve its performance. Toyir and coworkers studied Ga-promoted Cu-based catalysts on SiO₂ and ZnO supports and obtained high activity, selectivity, and stability for Cu-Zn-Ga/SiO₂ (hydrophobic silica) [13]. Methanol was the main product, with a selectivity of 99% and a conversion of 5.6% at 543 K. They found that Ga increased the activity and selectivity of the catalyst for methanol when compared to Cu/ZnO/Al₂O₃. In another

* Corresponding author.

E-mail address: maria.curetarana@upr.edu (M.C. Curet-Arana).

Table 1
Reactions involved in the hydrogenation of CO₂ and CO.

	Reaction	$\Delta H_{\text{rxn}}^{\circ}$ (kJ/mol)	Ref.
Methanol Synthesis from CO ₂	$\text{CO}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_3\text{OH}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	-50	[11,12]
Reverse Water Gas Shift	$\text{CO}_{2(\text{g})} + \text{H}_2(\text{g}) \leftrightarrow \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	41	[11]
Methanol Synthesis from CO	$\text{CO}_{(\text{g})} + 2\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_3\text{OH}_{(\text{g})}$	-91	[12]
Formic Acid Synthesis from CO ₂	$\text{CO}_{2(\text{g})} + \text{H}_2(\text{g}) \leftrightarrow \text{HCOOH}_{(\text{g})}$	15 ^a	
Formaldehyde Synthesis from CO	$\text{CO}_{(\text{g})} + \text{H}_2(\text{g}) \leftrightarrow \text{CH}_2\text{O}_{(\text{g})}$	-5	[42]
Formaldehyde Synthesis from CO ₂	$\text{CO}_{2(\text{g})} + 2\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_2\text{O}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	36 ^a	

^a Values calculated by using thermodynamic data provided from NIST [43].

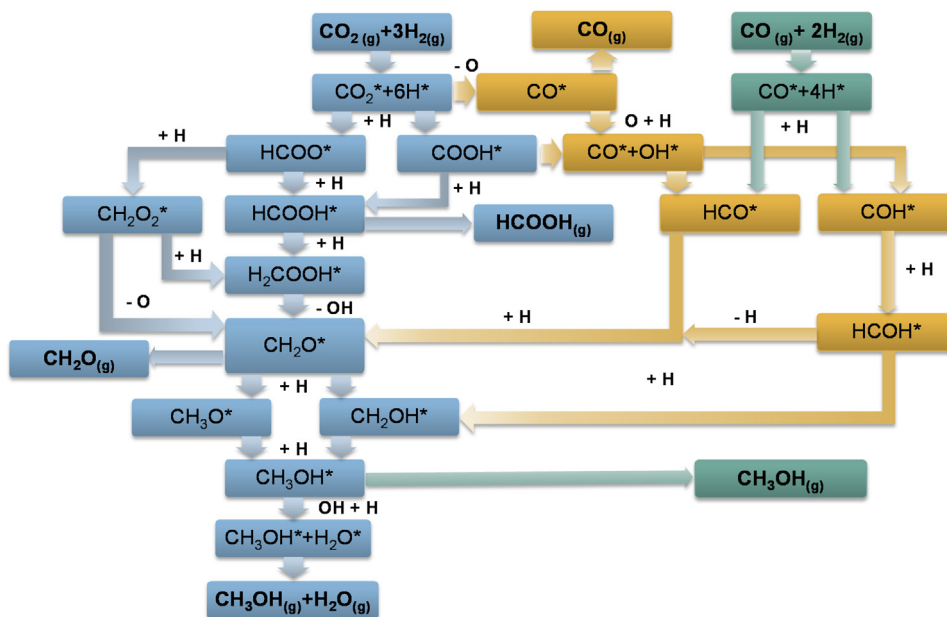


Fig. 1. Proposed reaction mechanisms for the hydrogenation of CO₂ and CO.

study, Toyir et al. also proved that the addition of Ga onto Cu/ZnO improved the catalyst stability [14]. In addition, they determined that higher Ga/Cu ratios increased the methanol production [13,14]. Melián-Cabrera and coworkers studied the effect of Pd incorporation on the performance of a CuO–ZnO catalyst for the methanol synthesis [15]. They found that there is a synergistic effect of Pd on the active Cu sites, and that Pd facilitates the H₂ spillover and transport of hydrogen to the active sites while maintaining CuO in a more reduced state. Nerlov et al. investigated the effect of CO in the methanol synthesis from CO₂ hydrogenation on the Cu(100) surface modified by Ni [16]. They reported that the methanol production increased when CO is fed into the reaction system, because CO activates the catalyst by inducing segregation of Ni to the surface. Studt and coworkers tested the catalytic performance of a CuNi alloy supported on silica in the hydrogenation of CO to methanol, obtaining similar turnover frequencies and slightly higher selectivities for methanol, when compared against the commercial Cu/ZnO/Al₂O₃ catalyst [17].

Catalysts based on other metals (e.g., Ni, Ga and Pd) have been also investigated and they have demonstrated to be potential promoters for the hydrogenation of CO₂ [10,18]. Recently, it has been demonstrated that a Ni-Ga intermetallic compound has better catalytic activity to reduce CO₂ and is more selective than Cu/ZnO/Al₂O₃ for methanol [10]. Fujitani et al. studied Pd-based catalysts for methanol production from CO₂ and H₂ and they reported that Pd/Ga₂O₃ was more active than Cu/ZnO on the basis of yields and turnover frequencies [18].

Some of these potential catalysts for the hydrogenation of CO₂ have been also investigated with density functional theory

(DFT) calculations. The adsorption and activation of CO₂ were theoretically studied on Cu-Ni bimetallic clusters by evaluating distinct metal compositions and geometry configurations in the clusters [19]. The authors found that the cluster with higher composition of Ni (Cu₄₂Ni₁₃) and the icosahedral conformation exhibited the highest adsorption of CO₂. Yang et al. investigated the effects of the metal dopants Pd, Au, Pt, Ni and Rh on the catalytic activity of Cu(111) for the methanol synthesis through CO₂ hydrogenation using DFT methods with kinetic Monte Carlo (KMC) simulations [20]. They determined that Ni, Pt, Pd, and Rh promote the CH₃OH synthesis reaction, while Au deactivates the reaction, being Ni/Cu(111) the surface with the best catalytic performance.

Experimental and theoretical observations indicate that CO₂ is chemically adsorbed on Ni(110) under UHV conditions [21]. Dissociative adsorption of CO₂ has been observed on Ni, Al and Mg surfaces [22]. Behrens and coworkers demonstrated, with DFT calculations that Zn substituted into the Cu(211) surface at the step sites increased the catalyst activity because it increased the adsorption strengths of the intermediates and decreased the energy barriers [8]. They proposed that the use of other promoters with the same oxophilicity of Zn might increase the catalytic activity of Cu. They reported that there is a synergistic effect between Cu and Zn, because Cu sites near Zn atoms serve as adsorption sites for oxygen-bound intermediates.

The hydrogenation of CO₂ and CO has been also studied by DFT methods to elucidate the elementary steps in the reaction mechanisms that have not been fully clarified. There are two major routes that have been proposed for the methanol synthesis from CO₂ hydrogenation: the formate (HCOO) pathway

Download English Version:

<https://daneshyari.com/en/article/64555>

Download Persian Version:

<https://daneshyari.com/article/64555>

[Daneshyari.com](https://daneshyari.com)