



# Quantum mechanical study of CO<sub>2</sub> and CO hydrogenation on Cu(111) surfaces doped with Ga, Mg, and Ti



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## ABSTRACT

DFT methods were used to analyze metal (M)-doped Cu(111) surfaces to identify surface alloys that could catalyze the hydrogenation of CO<sub>2</sub>. The adsorption of relevant species for CO<sub>2</sub>/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 CO<sub>2</sub>/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 CO<sub>2</sub> hydrogenation. CO<sub>2</sub> 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 CO<sub>2</sub> 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, CH<sub>2</sub>O, CH<sub>3</sub>O, and HCO are good descriptors for catalyst screening.

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## 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 CO<sub>2</sub> emissions to the atmosphere, the need for finding alternative carbon sources has sparked interest in using renewable sources. The conversion of CO<sub>2</sub> into valuable organic compounds promises to be a potential approach to reduce the environmental impact of CO<sub>2</sub> 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 CO<sub>2</sub>. Methanol is industrially produced from CO, H<sub>2</sub> and small amounts of CO<sub>2</sub> using Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> to methanol is an exothermic reaction, as described in Table 1 [11]. However, the hydrogenation of CO to methanol is even more exothermic than CO<sub>2</sub> hydrogenation [12]. Consequently, in addition to high pressures, relative low temperatures (> 240 °C) are required to favor the hydrogenation of CO<sub>2</sub> 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 CO<sub>2</sub>, different metal dopants or promoters have been previously studied to modify the conventional catalyst used for CO<sub>2</sub> hydrogenation and improve its performance. Toyir and coworkers studied Ga-promoted Cu-based catalysts on SiO<sub>2</sub> and ZnO supports and obtained high activity, selectivity, and stability for Cu-Zn-Ga/SiO<sub>2</sub> (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/Al<sub>2</sub>O<sub>3</sub>. In another

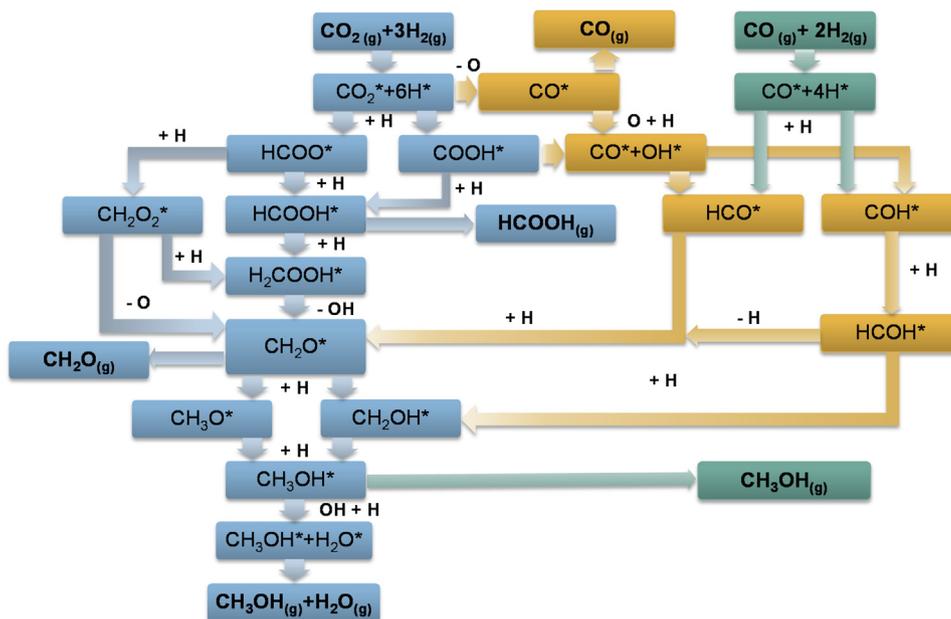
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**Table 1**  
Reactions involved in the hydrogenation of CO<sub>2</sub> and CO.

	Reaction	$\Delta H_{\text{rxn}}^{\circ}$ (kJ/mol)	Ref.
Methanol Synthesis from CO <sub>2</sub>	$\text{CO}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_3\text{OH}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	-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 <sub>2</sub>	$\text{CO}_{2(\text{g})} + \text{H}_2(\text{g}) \leftrightarrow \text{HCOOH}_{(\text{g})}$	15 <sup>a</sup>	
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 <sub>2</sub>	$\text{CO}_{2(\text{g})} + 2\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_2\text{O}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	36 <sup>a</sup>	

<sup>a</sup> Values calculated by using thermodynamic data provided from NIST [43].



**Fig. 1.** Proposed reaction mechanisms for the hydrogenation of CO<sub>2</sub> 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 H<sub>2</sub> 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 CO<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub> [10,18]. Recently, it has been demonstrated that a Ni-Ga intermetallic compound has better catalytic activity to reduce CO<sub>2</sub> and is more selective than Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> for methanol [10]. Fujitani et al. studied Pd-based catalysts for methanol production from CO<sub>2</sub> and H<sub>2</sub> and they reported that Pd/Ga<sub>2</sub>O<sub>3</sub> was more active than Cu/ZnO on the basis of yields and turnover frequencies [18].

Some of these potential catalysts for the hydrogenation of CO<sub>2</sub> have been also investigated with density functional theory

(DFT) calculations. The adsorption and activation of CO<sub>2</sub> 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 (Cu<sub>42</sub>Ni<sub>13</sub>) and the icosahedral conformation exhibited the highest adsorption of CO<sub>2</sub>. 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 CO<sub>2</sub> hydrogenation using DFT methods with kinetic Monte Carlo (KMC) simulations [20]. They determined that Ni, Pt, Pd, and Rh promote the CH<sub>3</sub>OH synthesis reaction, while Au deactivates the reaction, being Ni/Cu(111) the surface with the best catalytic performance.

Experimental and theoretical observations indicate that CO<sub>2</sub> is chemically adsorbed on Ni(110) under UHV conditions [21]. Dissociative adsorption of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> hydrogenation: the formate (HCOO) pathway

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