Title: Low Temperature CO₂ Hydrogenation to Alcohols and Hydrocarbons over Mo₂C Supported Metal Catalysts

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Abstract

A series of M/Mo₂C (M=Cu, Pd, Co and Fe) were synthesized and evaluated for CO₂ hydrogenation at 135-200 °C in liquid 1,4-dioxane solvent. The Mo₂C served as both a support and a co-catalyst for CO₂ hydrogenation, exhibiting turnover frequencies of 0.6×10^{-4} and $20 \times 10^{-4} \text{ s}^{-1}$ at 135 and 200 °C, respectively. Methanol was the major product at 135 °C, while CH₃OH, C₂H₅OH, and C₂₊ hydrocarbons were produced at 200 °C. The addition of Cu and Pd onto the high surface area Mo₂C enhanced the production of CH₃OH, while Co and Fe enhanced the production of C₂₊ hydrocarbons. Results for CO₂, CO, and CH₃OH hydrogenation experiments suggested that CO₂ was the primary source for CH₃OH while CO was the intermediate to hydrocarbons during CO₂ hydrogenation. Characterization of the spent M/Mo₂C catalysts revealed very little change in the surface and bulk chemistries and structures, indicating their stability in the liquid environment.

Key Words:

CO₂ hydrogenation; liquid phase reaction; molybdenum carbide supported catalysts; alcohol and hydrocarbon production

1. Introduction

Natural gas and petroleum are the principal resources used to produce most chemicals. In addition, the production of chemicals is among the most energy-intensive segments of the industrial sector, accounting for the consumption of ~5 quadrillion Btu per year within the United States [1], most of which comes from fossil fuels. Growing concerns about climate change and diminishing fossil resources are driving the development of renewable and non-fossil-based feedstocks for the production of chemicals. Carbon dioxide has attracted considerable attention as a C₁ building block for the production of chemicals and fuels [2-6]. With the advances in capture technologies, CO₂ could become available at low cost and its conversion to value-added chemicals could be cost-competitive [3]. Furthermore, large-scale CO₂ conversion could balance global CO₂ emissions. [7, 8]

Presently the conversion of CO₂ is limited to a few products including urea (146 Mton/year [9]), methanol via the reverse water gas shift (RWGS) then CO hydrogenation (5 Mton/year [10]) and salicylic acid (170 kTon/year [6]). The most promising strategy for the large-scale conversion of CO₂ is through hydrogenation processes, producing alcohols and hydrocarbons. [3, 11] However, CO₂ hydrogenation is quite challenging due to its stability, the lack of sufficiently active and selective catalytic materials, and the lack of cost-effective, non-fossil fuel sources of the hydrogen (e.g. via water splitting) [4]. This paper describes the development of novel catalytic materials for CO₂ hydrogenation at low temperatures where products like CH₃OH are preferred and in the liquid phase; it is noteworthy that there has been significant progress in water-splitting for H₂ production [12].

Carbon dioxide hydrogenation is commonly performed over oxide (e.g. SiO₂, Al₂O₃, TiO₂, and CeO₂) supported metal catalysts at temperatures ranging from 220 to 320 °C with gas phase reactants. The most active materials typically employ precious metals, which are expensive and often catalyze the formation of CO and CH₄, relatively low value products. For example, Au/TiO₂ [13] and Pt/CeO₂ [14] are reported to selectively produce CO via the RWGS reaction; Ru/Al₂O₃ [15] and Ni/SiO₂ [16] are active for CH₄ production; and Pd/CeO₂ [17] and Cu/ZnO [18] are active for CH₃OH synthesis. Many of these systems are considered bifunctional with the metal sites facilitating the dissociation of H₂ and the oxide

supports primarily facilitating C=O bond cleavage and accommodating surface intermediates. [19, 20]

Transition metal carbides (TMC) can exhibit catalytic properties that resemble those of precious metals [21] and are active for a number of reactions including CO hydrogenation [22], water-gas shift [23, 24], and methane reforming [25]. Importantly, these materials are active for CO₂ hydrogenation. Dubio et al. reported results for a series of TMC catalysts and showed that Mo₂C and Fe₃C were more active than WC and TaC at 220-280 °C [26]. However, more than 60% of the CO₂ was converted into CO and CH₄. They also reported that the addition of Cu to the Mo₂C and Fe₃C catalysts led to enhancements in the CH₃OH selectivities by more than 50%. Similar enhancements were described by Vidal et al. [27], using Cu or Au promoted TiC (001) to produce CH₃OH from CO₂ hydrogenation at 250 – 320 °C. The Cu/TiC (001) material exhibited a CH₃OH production rate that was an order of magnitude higher than that for the pure TiC (001) material. Xu et al. [28] described the use of Mo carbides, including α -MoC_{1-x} (x<0.5) and β -MoC_y (y~0.5), for CO₂ hydrogenation at 300 °C. They concluded that the reaction activity and selectivity were strong functions of the Mo/C ratio, however, CO and CH₄ accounted for ~70% of the products. Porosoff et al. [29] recently reported that a bulk Mo₂C catalyst outperformed CeO₂ supported Pt or Pd catalysts for CO₂ hydrogenation, producing primarily CO (~93% selectivity) at 300 °C and 1 atm. The addition of Co onto Mo₂C resulted in a slight increase in the CO selectivity.

Investigations of CO₂ hydrogenation over TMC-based and other types of catalysts have most often been carried out at relatively high temperatures (250-300 °C), where desirable products like CH₃OH are not thermodynamically favored. Fan et al. [30] reported results for CO₂ hydrogenation over Cu/ZnO and Cu/Cr₂O₃ catalysts at 200 °C with 7.5 bar of CO₂, 22.5 bar of H₂ and ethanol as the solvent. This lower temperature not only enhanced the selectivities to CH₃OH but decreased selectivities to CO (product of an endothermic reaction) [31]. The best-performing catalyst, Cu/ZnO, afforded a rate of 0.02 $\mu\text{mol}_{\text{CO}_2} \text{ m}^{-2}\text{s}^{-1}$ with selectivities to CH₃OH, CO and ethyl formate of 73, 20 and 6%, respectively. The results suggested that ethyl formate was an intermediate for the

production of CH₃OH. Huff and Sanford [32] developed a cascade system incorporating homogeneous catalysts for CO₂ hydrogenation through formic acid and formate intermediates, although incompatibility among the catalyst components inhibited overall performance. Yu et al. [33] reported the production of methyl formate from CO₂ in liquid methanol over a Cu/ZnO/Al₂O₃ catalyst. A rate of 0.05 $\mu\text{mol}_{\text{CO}_2} \text{m}^{-2}\text{s}^{-1}$ was achieved with 79% selectivity to methyl formate (balance CO) at 150 °C, 140 bar CO₂ and 20 bar H₂. They suggested that surface formate was a key intermediate. Inspired by these results, we recently explored the use of Mo₂C supported Cu catalyst for CO₂ hydrogenation at 135 °C, with 10 bar CO₂ and 30 bar H₂ in 1,4-dioxane [34]. The addition of Cu onto Mo₂C significantly enhanced the CH₃OH TOF ($2.0 \times 10^{-4} \text{ s}^{-1}$). Introducing ethanol reagent improved the CH₃OH production (by ~ 40%) as a consequence of enhanced formation of the formate intermediate.

Research described in this paper extends our investigation of CO₂ hydrogenation over nanostructured Mo₂C supported metal catalysts in liquid solvents to include other metals and temperatures higher than 135 °C. We also interrogated the reaction pathways by probing the systems with possible intermediates, including CO and CH₃OH. The use of liquid solvents, as opposed to reactions in gas phase, can impact catalyst stability [35]. For example, Verhoeof et al. [36] reported that MCM-41 supported heteropoly acid catalysts were susceptible to severe deactivation during liquid phase esterifications compared to carrying out these reactions in the gas phase. This deactivation was primarily due to the presence of water which enhanced the mobility of the heteropoly acid species and caused catalyst sintering [36]. Therefore, we also investigated stabilities of the M/Mo₂C catalysts by comparing the surface and bulk, physical and chemical properties before and after reaction. The findings will enhance our understanding of Mo₂C-supported metal catalysts for low temperature CO₂ hydrogenation and provide a scientific basis for their rational design for other related applications.

2. Materials and Methods

2.1 Catalyst Preparation

The bulk Mo₂C catalyst was prepared using a temperature programmed reaction (TPR) technique starting from an ammonium molybdate (AM) precursor, (NH₄)₆Mo₇O₂₄•4H₂O (Alfa Aesar). Approximately 1.3g of AM was sieved to 125-250 μm and then loaded into a quartz tube reactor. The AM was treated in H₂ flowing at 400 mL/min for 70 min, as the temperature was increased from 25 to 350 °C and held at 350 °C for 12 h. The reaction gas was then switched to 15% CH₄/H₂ (400 mL/min) while the temperature was increased to 590 °C in 1.5 h and maintained at 590 °C for 2 h; the reactor was then immediately quenched to room temperature. The Cu/Mo₂C and Pd/Mo₂C catalysts were prepared using a wet impregnation method described elsewhere [37]. Briefly, the freshly-synthesized Mo₂C was transferred under 15% CH₄/H₂ gas into a beaker containing 70 mL deaerated water (to avoid the oxidation of Mo₂C) with target amounts of Cu(NO₃)₂ and Pd(NO₃)₂•4NH₃ and allowed to interact for 20 h to achieve the 5 wt% nominal metal loading. Argon was continuously purged through the solutions during the wet impregnation process to deaerate and agitate the solution. This method enabled the metal precursor to directly interact with the native Mo₂C surface (as opposed to a passivated material). A recently study by Wyvratt et al. reported that deposition of active metal onto the native Mo₂C produced nanoscale metal domains that were better-dispersed than those deposited onto a passivated Mo₂C surface, resulting in superior catalytic performance for the WGS reaction [38]. It has also been suggested by Schaidle et al. that Cu and Pd are deposited onto the Mo₂C via electrostatic adsorption and both metals are reduced in-situ by the Mo₂C support during the wet impregnation process [37]. The resulting catalyst slurry was dried at 110 °C for 2 h and reduced in flowing H₂ (400 mL/min) at 300 °C for 4 h to decompose the nitrate and produce the Cu or Pd domains. The Co/Mo₂C and Fe/Mo₂C catalysts were synthesized using the incipient wetness impregnation. The impregnation was performed using an aqueous solution containing target amount of Co(NO₃)₂ or Fe(NO₃)₃, on the Mo₂C support with a pore volume of 0.13 cm³/g (measured by N₂ physisorption). The incipient wetness was applied because only small amounts of Co and Fe (< 2 wt%) could be deposited via electrostatic adsorption [37]. The freshly synthesized Mo₂C was transferred under Argon to a water-tolerant, oxygen free glovebox filled with N₂ to avoid any bulk or surface oxidation of Mo₂C. The resulting catalysts were dried in the glovebox on a heating

plate at 110 °C for 2 h and then transferred under Argon into a quartz reactor where they were reduced in flowing H₂ (400 ml/min) for 4 h at 450 °C to produce the Fe and Co domains.

2.2 Catalyst Characterization

Surface areas of the materials were determined from N₂ physisorption based on the BET method using a Micromeritics ASAP 2010 analyzer. The Horvath–Kawazoe method was used to determine the pore size distributions. All of the Mo₂C-based catalysts were degassed (< 5 mm Hg) at 350 °C for 4 h prior to the surface area measurements. The bulk crystalline structures were characterized using X-ray diffraction (Rigaku Miniflex 600) with 2 θ ranging from 10° to 90° and a scan rate of 5 °/min. Crystallite sizes were estimated via line broadening analysis using the Scherrer equation [39]. Scanning electron microscopy (SEM) for select catalysts were performed using FEI Nova Nanolab Dualbeam (FIB/SEM). To enhance the conductivity, the materials were gold sputter coated prior to imaging. Elemental analyses were carried out using Energy Dispersive X-ray Spectroscopy (EDX). All the materials were passivated in 1% O₂/He for 5 h before performing SEM in order to be loaded into the sample chamber without bulk oxidation. Metal compositions for the M/Mo₂C catalysts were determined by inductively coupled plasma (ICP-OES) using a Varian 710-ES analyzer.

The surface site densities for Mo₂C-based catalysts were determined via CO chemisorption using a Micromeritics AutoChem II 2920 system with a thermal conductivity detector. The Mo₂C-based catalysts were passivated in order to be loaded into the reactor chamber equipped with the AutoChem II 2920 system. Prior to the measurements, the catalysts were recarburized in 15% CH₄/H₂ for 4 h at 590 °C, then degassed in He at 600 °C for 1 h. The catalysts were then cooled to 25 °C and repeatedly dosed with 5% CO/He (5 mL sample loop) until reaching saturation. Deconvolution of contributions from the metal and Mo₂C is desired, however, it is difficult because CO can adsorb to both the metal and Mo₂C. Nevertheless, as Mo₂C accounts for 95 wt% of the catalyst, the CO chemisorption uptakes should provide reasonable estimates of site densities. The catalyst surface coverage were estimated by assuming a 10¹⁹ active sites/m² for the Mo₂C support [24]. The H₂ temperature-programmed reduction (H₂-TPR) was also

carried out using the Micromeritics AutoChem II 2920 system. The passivated M/Mo₂C catalysts were first purged with He with a flow rate of 70 ml/min at 200 °C for 2 h and then were cooled to room temperature. The H₂-TPR was then conducted in 10% H₂/Ar by increasing the temperature from room temperature to 800 °C at a heating rate of 4 °C/min, where the H₂ consumption was recorded as a function of temperature.

2.3 Reaction Rates and Selectivities

The activity measurements were performed in a 50 mL Parr Instruments reactor (Micro 5500). The reactor system was equipped with a programmable temperature controller and a magnetic drive for the impeller. The gas phase reactor effluent was analyzed using gas chromatography (Varian 450 with flame ionization and thermal conductivity detectors). Liquid samples (0.4 mL) were periodically withdrawn during the reaction using a dip tube, which was equipped with a 20 µm filter to separate the liquid from the solid catalyst particles. The liquid samples were analyzed offline using gas chromatography (Varian 450 with flame ionization detector).

The Mo₂C-based catalysts were used as synthesized without passivation. To avoid contact of the materials with air, they were transferred under an inert atmosphere and stored in an Ar filled glovebox (Mbraun UNIlab, H₂O < 0.1 ppm, O₂ < 5ppm). Solvents for the reactions contained 37.5 mL 1,4-dioxane (anhydrous, Acros Organics) and 10 µL n-decane (Acros Organics) as an internal standard. For the CO₂ hydrogenation experiments, the reactors were charged with 10 bar CO₂ and 30 bar H₂ through a dip tube after purging the solvents with H₂ for 15 min to remove dissolved oxygen at temperatures of 135-200 °C. Under these conditions, the solubilities for CO₂ and H₂ are approximately 1.5 and 0.14 mol/L at 135 °C and 1.0 and 0.18 mol/L [40, 41] at 200 °C, respectively, in 1,4-dioxane. The CO₂ reaction rates were calculated based on formation rates for the products (on a C₁ basis) after 2 h. Carbon balances closed to within ± 8% for the experiments. The turnover frequency (TOF) was determined by normalizing the rate by the CO uptakes. The

selectivity is defined as the molar ratio of a specific product over the total products on a C₁ basis.

For select catalysts, CO hydrogenation and CH₃OH hydrogenation were performed at 200 °C to investigate the reaction pathways. For CO hydrogenation the reactant was 10 bar CO and 30 bar H₂ in 37.5 ml 1,4-dioxane. The CH₃OH hydrogenation experiments were performed using 7 mmol (~0.3 ml) CH₃OH, 10 bar N₂ (used as an inert gas to balance the pressure) and 30 bar H₂ in 37.2 ml 1,4-dioxane. A catalyst loading of 200 mg was used for each experiment unless stated otherwise. The reactor was heated at a rate of 5 °C/min from room temperature to the target reaction temperature, and then agitated at a constant rate of 300 rpm, which indicated the start of the reaction.

Several of the spent catalysts were recovered for characterization. To avoid contact with air, the materials were removed from the reactor (as catalyst slurry) in the Ar-filled glovebox and dried in vacuum for 2 h at room temperature in the glovebox antechamber. The dried catalysts were collected and stored in the glovebox before they were characterized. Similar weights were measured for the recovered catalysts, suggesting minimal catalyst loss during the reaction.

3. Results

3.1 Pre-Reaction Catalyst Properties

The metal contents, surface areas, site densities, and corresponding theoretical surface coverages for all of the catalysts are listed in Table 1. Metal contents for each of the M/Mo₂C catalysts were ~5 wt%, the target loading. The deposition of metals onto Mo₂C caused a slight decrease in the surface areas, possibly due to pore blocking by the metal particles. Pore size distributions for the M/Mo₂C and bulk Mo₂C materials suggested that the metal particles primarily blocked micropores in the Mo₂C support (Fig. S1). Site densities for the M/Mo₂C materials were lower than that for the bulk Mo₂C (~1.6 molecules_{CO}/nm²) with the Pd/Mo₂C catalyst possessing the highest site density and lowest nominal surface coverage owing perhaps to the high atomic mass of Pd. For comparison, site densities for Cu [42], Pd [43, 44], Co [45, 46], and Fe [47, 48] have been reported to be 4.9, 6.6, 7.4, and 12.1 molecules_{CO}/nm², respectively. The lower site densities for the

M/Mo₂C catalysts suggest that metal-Mo₂C interactions suppressed CO adsorption on Mo₂C. Similar reductions in CO adsorption capacities have been reported for a Pt/Mo₂C catalyst prepared using methods similar to those described in our paper [37].

Table 1. Physical properties of the M/Mo₂C catalysts.

Catalysts	Metal Content (wt%)	Surface Area (m ² /g)	Site Density (μmol/g)	Surface Coverage (ML%) ^a
Mo ₂ C	N/A	151	406	N/A
Cu/Mo ₂ C	5.3	135	298	35.1
Pd/Mo ₂ C	5.2	138	346	20.6
Co/Mo ₂ C	5.5	124	305	39.4
Fe/Mo ₂ C	5.1	118	306	38.4

^a Calculated assuming 10¹⁹ sites/m² of Mo₂C support. ML = monolayer.

X-ray diffraction patterns for the catalysts are shown in Figure 1. The Mo₂C support contained a mixture of α-MoC_{1-x} (x ~0.5) and β-Mo₂C in approximately equal amounts (quantified by Whole Pattern Fitting Rietveld Refinement) and there was no evidence of Mo oxides. This finding indicated a complete carburization of Mo oxide precursor during the synthesis process. Given the Mo:C ratio for the material, we will refer to the Mo carbide as Mo₂C. Diffraction patterns for the M/Mo₂C catalysts resembled that for the bulk Mo₂C with no discernable peaks for the supported metals. This observation was likely due to the fact that the most significant peaks associated with the metals overlapped with the Mo₂C peaks (Fig. S2). For example, the Cu (111) peak at ~43° and Pd (111) peak at ~40 ° are located near the most intense peaks for α-MoC_{1-x} and β-Mo₂C, respectively. Weak peaks for the metals in the XRD pattern could also be a consequence of the small crystallite dimensions; the detection limit is approximately 5 nm.

Figure 1. X-ray diffraction patterns for Mo_2C , $\text{M}/\text{Mo}_2\text{C}$, and standards.

3.2 CO_2 Hydrogenation

The CO_2 hydrogenation reaction rates and selectivities for the Mo_2C and $\text{M}/\text{Mo}_2\text{C}$ catalysts are summarized in Table 2. At 135 °C, CH_3OH was the major product with selectivities in excess of 79%, while CO and CH_4 were produced in small quantities. The deposited metals moderately enhanced the CO_2 conversion rates and CH_3OH selectivities. Very small but measurable amounts of C_2H_6 and C_3H_8 were observed for the $\text{Co}/\text{Mo}_2\text{C}$ and $\text{Fe}/\text{Mo}_2\text{C}$ catalysts. When the temperature was increased to 200 °C, the CO_2 conversion rate increased by more than an order of magnitude. We also observed a significant shift in product distributions with C_1 - C_4 hydrocarbons produced over all of the catalysts. There was also a concomitant decrease in the selectivity to CH_3OH on increasing the temperature to

200 °C (50-70%) compared to that at 135 °C (80-95%). This reduction in selectivity was

Table 2. CO₂ hydrogenation rates and selectivities over Mo₂C and M/Mo₂C catalysts.^a

Catalysts	T _{rxn} (°C)	CO ₂ Conv. Rate/TOF ^b		Selectivity (%) ^{c,d}						
		umol/m ² /s•10 ⁴	s ⁻¹ •10 ⁴	MeOH	EtOH	CO	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃₊
Mo ₂ C	135 ^e	1.7	0.6	79	0	16	5.3	0	0	0
	200	55	20	53	16	4.9	17	0.8	5.0	3.0
Cu/Mo ₂ C	135 ^e	4.6	2.1	93	0	4.1	2.6	0	0	0
	200	90	41	63	14	8.6	9.8	0.3	3.7	1.9
Pd/Mo ₂ C	135	5.9	2.3	95	0	3.6	1.6	0	0	0
	200	97	39	68	11	9.6	7.6	0.3	2.5	1.3
Co/Mo ₂ C	135	4.8	1.9	84	0	5.7	9.4	0	1.1	0.1
	200	86	35	46	25	9.5	9.5	0.6	5.6	1.4
Fe/Mo ₂ C	135	3.9	1.5	87	0	4.1	7.2	0	1.2	0.6
	200	99	38	58	16	6.8	8.1	0.4	6.3	3.8

a. 10 bar CO₂, 30 bar H₂, 37.5 ml 1,4-dioxane and 200 mg catalyst.

b. Calculated at 2 h.

c. Calculated at ~ 1.0 % CO₂ conversion at 135 °C and ~ 10% CO₂ conversion at 200 °C. The selectivities were calculated on a C₁ basis.

d. C₃ contains C₃H₆ and C₃H₈, C₄ contains C₄H₈ and C₄H₁₀.

e. Rate data taken from [34].

anticipated as CH₃OH synthesis is a highly exothermic reaction ($\Delta H_{25^\circ\text{C}} = -49.5$ kJ/mol).

Figure 2 compares TOFs for alcohol formation over the M/Mo₂C catalysts at 135 and 200 °C. The CH₃OH TOFs at 135 °C decreased in the following order: Pd/Mo₂C $\approx$ Cu/Mo₂C > Fe/Mo₂C > Co/Mo₂C > Mo₂C; the similar trend was also observed for CO₂ hydrogenation at 200 °C (Figure 2). In addition to CH₃OH, C₂H₅OH was produced at 200 °C. Interestingly, when taken together, the CH₃OH and C₂H₅OH TOFs for all of the M/Mo₂C catalysts were similar ($26\text{-}30 \times 10^{-4} \text{ s}^{-1}$). A potential pathway to C₂H₅OH and roles of the metals will be discussed in later sections.

Figure 2. Turnover frequencies of methanol and ethanol formation at (a) 135 °C and (b) 200 °C on M/Mo₂C catalysts. Experiments were performed at 10 bar CO₂, 30 bar H₂, and 37.5 ml 1,4-dioxane.

Figure 3 compares TOFs for CO and hydrocarbon formation at 135 and 200 °C. At

135 °C, the addition of Cu or Pd to Mo₂C had very small effects on the CO and

hydrocarbon formation rates, while the addition of Fe and Co resulted in a decrease in CO formation and increase in hydrocarbon formation; mostly CH₄ and small amounts of C₂H₆ and C₃H₈. Similarly, at 200 °C, Cu and Pd had very small effects on the production of CO

Figure 3. Turnover frequencies of CO and hydrocarbon formation at (a) 135 °C and (b) 200 °C on M/Mo₂C catalysts. Experiments were performed at 10 bar CO₂, 30 bar H₂, and 37.5 ml 1,4-dioxane.

and hydrocarbon compared to that for bulk Mo₂C catalyst, suggesting these metals were not active for the production of hydrocarbons. In contrast, the deposition of Fe and Co onto Mo₂C significantly enhanced the production of C₂-C₄ hydrocarbons, while decreasing the selectivity to CO. The hydrocarbons were primarily paraffins, with an olefin/paraffin ratio of 0.08 – 0.35 (see Fig. S3). Such low olefin/paraffin ratios have also been reported for other Mo₂C-based materials [26, 49]; this observation is also consistent with the high hydrogenation activities associated with Mo₂C. Addition of the metal did not significantly affect the olefin/paraffin ratios.

3.3 Reaction Pathway Investigation

There are multiple pathways to the products described in the last section. The CO_2 hydrogenation products could be the result of CO produced via the RWGS reaction. Mo_2C catalysts have been reported to be highly active for RWGS [50]. Alcohols and hydrocarbons could be produced from CO. Alternately the alcohols and hydrocarbons may have been produced directly from CO_2 . Apparent activation energies for individual products often provide useful insights regarding the reaction pathways. We also used CO and CH_3OH as the reactants to interrogate the reaction pathways. Based on the activities and selectivities presented in Section 3.2, we selected the $\text{Cu}/\text{Mo}_2\text{C}$ (selective for CH_3OH) and $\text{Fe}/\text{Mo}_2\text{C}$ (selective for $\text{C}_2\text{-C}_4$ hydrocarbon) catalysts for the reaction pathway investigations.

Arrhenius plots for the formation of CH_3OH and hydrocarbons for the $\text{Cu}/\text{Mo}_2\text{C}$ and $\text{Fe}/\text{Mo}_2\text{C}$ catalysts are illustrated in Figure 4. The experiments were performed at each temperature using new catalysts (all from the same synthesis batch). The corresponding apparent activation energies, $E_{a,\text{App}}$, are listed in Table 3. Activation energies for hydrocarbon formation were very different and much higher than those for CH_3OH formation. This suggested that the rate determining steps involved different intermediates and perhaps different active sites. In comparing $E_{a,\text{App}}$ values for Mo_2C with those for the supported metal catalysts, we noted a slight reduction consistent with the metal facilitating

Figure 4. Arrhenius plots for the formation of (a) CH_3OH and (b) $\text{C}_1\text{-C}_4$ hydrocarbons from CO_2 hydrogenation at temperatures of 135–200 °C on Mo_2C , $\text{Cu}/\text{Mo}_2\text{C}$, and $\text{Fe}/\text{Mo}_2\text{C}$. The experiments were performed at temperatures of 135, 155, 175, 200 °C, 10 bar CO_2 , and 30 bar H_2 in 1,4-dioxane.

conversion. These trends are consistent with our previous findings that Cu facilitates methanol production while Fe enhances hydrocarbon formation over Mo₂C surface.

Table 3. Apparent activation energies for the Mo₂C and M/Mo₂C catalysts

Catalysts	E _{a,App} (kJ/mol) ^a	
	CH ₃ OH Formation	Hydrocarbon Formation
Mo ₂ C	76 ± 7	110 ± 8
Cu/Mo ₂ C	60 ± 5	105 ± 8
Fe/Mo ₂ C	65 ± 4	96 ± 7

^a E_{a, App} was calculated based on the reaction rates at 135-200 °C

3.3.1 CO Hydrogenation

The hydrogenation of CO was performed at 200 °C using 10 bar CO, 30 bar H₂ over Cu/Mo₂C and Fe/Mo₂C catalysts. The product formation TOFs are shown in Figure 5. For both the Cu/Mo₂C and Fe/Mo₂C catalysts, CH₃OH and C₂H₅OH were observed. The CH₃OH produced during CO hydrogenation was only 7.7 and 3.2% of that produced during CO₂ hydrogenation over these catalysts, respectively. This result suggested that most of the CH₃OH produced during CO₂ hydrogenation was directly from CO₂. The hydrocarbon formation TOFs from CO were 3-4 times higher than those from CO₂ hydrogenation, perhaps due to a higher CO concentration (by about a factor of 4) compared to the CO₂ concentration. Interestingly, when normalized by the CO concentrations, the hydrocarbon formation rates were comparable (within ±12%) for CO and CO₂ hydrogenation, again suggesting that the hydrocarbons were primarily produced via CO hydrogenation. In addition, the dominant product was CO₂ for both catalysts, suggesting the significance of WGS at these conditions. We will compare the chain propagation properties in the discussion section.

Figure 5. Product TOF for CO hydrogenation over Cu/Mo₂C and Fe/Mo₂C catalysts. (a) CO₂ and alcohol TOF (b) hydrocarbon TOF. Experiments were performed at 200 °C, 10 bar CO, 30 bar H₂, and 37.5 ml 1,4-dioxane.

3.3.2 CH₃OH Hydrogenation

The CH₃OH hydrogenation experiments were performed at 200 °C with 7 mmol of CH₃OH, 30 bar H₂, and 10 bar N₂ over the Cu/Mo₂C and Fe/Mo₂C catalysts. The only detectable product was CH₄ (See Fig. S4 in the SI), a consequence of CH₃OH hydrodeoxygenation (HDO) as shown in Eq. (1).

Early transition metal carbides including Mo₂C are known to be highly active HDO catalysts [51]. Although CH₃OH HDO is thermodynamically favorable, it is an undesirable side reaction, as CH₄ and H₂O are less valuable than CH₃OH and H₂. The normalized

CH₃OH consumption rate only accounted for 3~5% of CH₃OH produced during CO₂ hydrogenation, suggesting that only a small portion of the CH₃OH was lost via HDO. The Cu/Mo₂C was twice as active as the Fe/Mo₂C catalyst (Fig. S4) for CH₃OH HDO with Cu being more effective in producing CH₄. The results also indicated that CH₃OH was not an intermediate for the production of C₂-C₄ hydrocarbons. The amount of CH₄ produced from CH₃OH HDO was negligible (0.7-1%) compared to the total CH₄ formation during the CO₂ hydrogenation. Neither CO nor CO₂ were observed, indicating that methanol steam reforming (MSR) was insignificant under the conditions employed. This was not unexpected given the high H₂ and low H₂O concentrations used in our experiments; note that anhydrous 1,4-dioxane (the solvent used in our experiments) can contain up to ~100 ppm water.

3.4 Post-Reaction Catalyst Properties

To evaluate the stabilities of M/Mo₂C catalysts, several physical and surface properties were characterized before (pre-reaction) and after (post-reaction) use for CO₂ hydrogenation. Again, the Cu/Mo₂C and Fe/Mo₂C catalysts were characterized. There were negligible differences in the surface areas and metal contents before and after reaction (Table 4). Diffraction patterns for the pre- and post-reaction Cu/Mo₂C and Fe/Mo₂C catalysts (Fig. S7) were similar although the post-reaction Cu/Mo₂C catalyst exhibited a slightly sharper peak at 43°, corresponding to Cu (111). This result suggested a small degree of sintering for the Cu/Mo₂C catalyst. Nevertheless, the results indicated the robustness of the Cu/Mo₂C and Fe/Mo₂C catalysts.

Table 4. Surface areas and metal contents for pre- and post-reaction Cu/Mo₂C and Fe/Mo₂C catalysts.

Catalysts	Surface Area (m ² /g)		Metal Contents (%)	
	pre-reaction	post-reaction	pre-reaction	post-reaction
Cu/Mo ₂ C	135 ± 4	129 ± 3	5.3 ± 0.4	5.5 ± 0.7
Fe/Mo ₂ C	118 ± 3	116 ± 2	5.1 ± 0.5	5.2 ± 0.4

Micrographs of the passivated, pre- and post-reaction Cu/Mo₂C and Fe/Mo₂C catalysts are illustrated in Figure 6. For the pre-reaction Cu/Mo₂C catalyst (Figure 6a), Cu was dispersed unevenly over the Mo₂C surface with particle sizes ranging from 30-500 nm. For the post-reaction Cu/Mo₂C catalyst, slightly larger Cu particles were observed ranging from 50-750 nm. This result confirmed some degree of sintering for the Cu particles during CO₂ hydrogenation at 200 °C. In contrast, the Fe/Mo₂C catalyst contained relatively large patches of Fe (3-10 μm). These patches are likely the cause for the decrease in the surface area by ~20% (Table 1). There was no significant change in the surface morphology when comparing the pre- and post-reaction Fe/Mo₂C catalysts. Interestingly, although Fe or Cu particle sizes observed in the micrographs were substantially larger than the XRD detection limit (~ 5nm), no discernable metal peaks were observed in the diffraction patterns. A plausible explanation is that Fe is part of either γ-Fe or Fe₂O₃, where their most significant peaks overlap with the major peaks of Mo₂C at ~41° and 37° respectively, making phase deconvolution difficult (Fig. S2); Cu (111) overlapped with α-MoC_{1-x} at 43° as shown in Figure 1. The large particles could also be agglomerates of small metal crystallites that were below the XRD detection limit. It has been reported that during the FTS, the active phase for the Fe-based catalyst is an iron carbide [52-54]. No obvious iron carbides were observed from the XRD, although one of the major Fe₂C peaks also overlaps with the Mo₂C peak at 43° (Fig. S2). From the EDX data (see Fig. S6), the carbon and iron were not co-located suggesting that Fe₂C was not present. Interestingly, oxygen and iron were co-located, which implicated the presence of Fe₂O₃ at least at the surface for the passivated materials.

Figure 6. Scanning electron micrographs for (a) pre-reaction Cu/Mo₂C, (b) post-reaction Cu/Mo₂C, (c) pre-reaction Fe/Mo₂C, and (d) post-reaction Fe/Mo₂C catalysts.

The H₂-TPR profiles for passivated pre- and post-reaction Cu/Mo₂C and Fe/Mo₂C catalysts are shown in Figure 7. The bulk Mo₂C catalyst produced two major peaks: one at low temperature ~ 210 °C that we attributed to reduction of the passivation layer [55], and a high temperature peak at ~ 700 °C which corresponded to decomposition of the Mo₂C, as observed previously [23]. The addition of Cu and Fe caused a shift in the lower temperature peak from 210 °C to 170 and 140 °C, respectively. A similar shift has been reported for Pt/Mo₂C catalysts prepared using methods similar to those described in this paper [56]. This was likely due to H₂ activation over the supported metal; subsequently this hydrogen could be used to reduce the passivated Mo₂C [57, 58]. The presence of the supported metals did not appear to affect decomposition of the Mo₂C (~700 °C). Similar H₂-TPR profiles were observed for the pre- and post-reaction catalysts, indicating that exposure to the reactants and solvent during the reaction did not alter surface chemistries of the M/Mo₂C catalysts.

Figure 7. H₂ consumption during the H₂-TPR experiment for the M/Mo₂C pre- and post-reaction catalysts. Conditions: 10% H₂/Ar, 4°C/min heating rate.

We also characterized the post-reaction catalysts by rerunning the CO₂ hydrogenation experiments. These experiments also provided an assessment of the recyclabilities of the catalysts. The results for the Cu/Mo₂C and Fe/Mo₂C catalysts are

Figure 8. Product TOFs for (a) Cu/Mo₂C and (b) Fe/Mo₂C over the fresh and reused catalysts.

shown in Figure 8. The slight decrease in CH₃OH production over the Cu/Mo₂C catalyst was consistent with the Cu sintering observed by XRD and SEM. The Fe/Mo₂C activity remained fairly constant on re-use.

4. Discussion

Results presented in this paper allow us to understand the effects of the metal type and temperature on the performance of Mo₂C supported metal catalysts for CO₂ hydrogenation, and the potential reaction pathways for these catalysts.

There are limited reports regarding CO₂ hydrogenation over Mo₂C-based catalysts, and other than our prior work [34], the experiments were carried out with gas phase reactants. Table 5 compares results from our work with those in the literature that are at similar temperatures. The CO₂ conversion TOFs measured during the liquid phase experiments were slightly lower than those for the gas phase. According to Bussche et al. [59], the rate for the gas phase CO₂ hydrogenation was first order with respect to both CO₂ and H₂. If the liquid phase reactions also followed the same rate law, the trend in CO₂ conversion TOFs could be a consequence of the relatively lower CO₂ and H₂ gas concentrations in the liquid phase compared to that in the gas phase. The concentrations for CO₂ and H₂ were 1.0 [41] and 0.18 mol/L[40] respectively in 1,4-dioxane and 0.3, 0.8 mol/L in the gas phase at 200 °C, 10 bar CO₂, and 30 bar H₂. We also observed that CO and CH₄ were the predominant products for CO₂ hydrogenation in the gas phase, while alcohols including C₂H₅OH and C₂₊ hydrocarbons were the predominant products for our work in the liquid phase. This difference in selectivity was likely due to the different reactant densities in the liquid and gas phase media. Different synthesis and pretreatment protocols could also contribute to the differences. Recall that we directly employed freshly-synthesized Mo₂C catalyst without surface passivation. Xu et al. [28] and Dubois [26] et al. described a pretreatment of the passivated Mo₂C via recarburization or H₂ reduction prior to the reaction. This could introduce different types or distributions of the active sites over the Mo₂C surface and ultimately alter the product selectivities.

Table 5. Comparing CO₂ hydrogenation activities and selectivities on Mo₂C-based catalysts from the literature and this study.

Catalyst	T (°C)/ P(bar)	CO ₂ /H ₂ ratio	Phase	TOF (s ⁻¹ •10 ⁴)	Selectivity (%)					Reference
					CO	CH ₃ OH	C ₂ H ₅ OH	CH ₄	C ₂₊	
Mo ₂ C	200/40	0.33	Liquid	20	5	53	16	17	9	This work
Cu/Mo ₂ C	200/40	0.33	Liquid	41	9	62	14	10	6	This work
Fe/Mo ₂ C	200/40	0.33	Liquid	38	7	58	16	8	11	This work
α-MoC _{1-x}	200/20	0.2	Gas	14	52	28	1	11	5	[28]
β-Mo ₂ C	200/20	0.2	Gas	106	39	21	1	29	8	[28]
Cu/Mo ₂ C	220/60	3	Gas	219	49	32	0.4	14	4	[26]

Results presented in this paper are consistent with different active sites for the formation of alcohols and hydrocarbons. Recall that activation energies obtained for methanol (60-76 kJ/mol) and hydrocarbons (96-110 kJ/mol) were different (Table 3), implying different rate determining steps and perhaps different pathways. Xu et al. [28] indicated that selectivities during CO₂ hydrogenation were highly dependent on the Mo/C ratio and crystalline phases present. They reported that β-Mo₂C catalyst was more active than α-MoC_{1-x} but produced primarily CO and CH₄, while α-MoC_{1-x} catalyst was more selective to CH₃OH. Porosoff et al. [29] also reported that a β-Mo₂C catalyst exhibited high selectivities to CO albeit at atmospheric pressure. Recall that the Mo₂C used in the current study was a mixture of α-MoC_{1-x} and β-Mo₂C, therefore, it is plausible that α-MoC_{1-x} produced primarily CH₃OH, and β-Mo₂C produced primarily CO (via RWGS) and perhaps C₁-C₄ hydrocarbons via FTS. The supported metals likely influenced the properties of sites already on the Mo₂C surface; it is also possible that the metals introduced new sites. Previously we reported experimental and computational results suggesting that, for Pt/Mo₂C catalysts, highly active sites for WGS were located at the interface between the Pt and Mo₂C [24]. These sites were much more active than those associated solely with Mo₂C or Pt. Results presented in this current paper do not allow us to determine if there were active sites for CO₂ hydrogenation at the interface between the metal and Mo₂C, however, the presence of the supported metal clearly contributed to the catalytic properties.

The addition of Cu and Pd resulted in a significant increase in the CO₂ conversion rates and selectivities to CH₃OH at 135 and 200 °C (Table 2). Copper [31, 60, 61] and Pd [62-64] are known to be selective for CO₂ hydrogenation to CH₃OH, and their addition to Mo₂C would be expected to improve the CH₃OH selectivity. Copper and Pd have also been reported to function synergistically with metal oxides (e.g. ZrO₂ and ZnO) by facilitating H₂ dissociation, which makes atomic H available to the support (likely via H₂ spillover) for CO₂ hydrogenation [65, 66]. The possibility of synergy between Cu and Mo₂C is currently being explored. While Cu and Pd affected CH₃OH selectivities, the Co/Mo₂C and Fe/Mo₂C catalysts yielded significant amounts of C₂₊ hydrocarbons and ethanol. Weatherby [67] reported that oxide supported Co and Fe facilitate the formation of C₂₊ products during CO₂ hydrogenation and suggested that the hydrocarbons were produced via CO hydrogenation. Our results are consistent with this finding, in particular that CO is likely a primary intermediate for hydrocarbons over the Mo₂C catalyst. We postulate that Mo₂C produces CO via the RWGS and CO hydrogenation occurs on both the Fe or Co particles [68-70] and the Mo₂C surface. Previously, it has been reported that CO adsorption site densities for the pure metals decreased in the following order: Fe>Co>Pd>Cu [42-48]. The higher CO hydrogenation activities for the supported Fe and Co catalysts may be a consequence of their higher CO surface coverages for these metals compared to those for the other metals. Ethanol may have been produced via a CO-insertion or oxygenate-based mechanism [49].

Figure 9 summarizes what we understand about the reaction pathways for CO₂ hydrogenation over Mo₂C supported metal catalysts under the experimental conditions employed for our research. Similarities between the hydrocarbon formation rates and

Figure 9. Proposed reaction pathways to produce alcohols and hydrocarbons from CO₂ and H₂. The solid arrows denote major pathways and the dashed arrows denote minor pathways. The pathways are applicable to the following experimental conditions: 200 °C, 10 bar CO₂, and 30 bar H₂ in 1,4-dioxane.

distributions for CO hydrogenation and CO₂ hydrogenation are consistent with CO being a common intermediate.

A useful way to compare the hydrocarbon distributions is via Anderson-Schulz-Flory chain propagation probabilities (α). These α values were determined using the Anderson-Schulz-Flory equation (Equation (1)):

$$W_n/n = (1 - \alpha)^2 \cdot \alpha^{n-1} \quad \text{Eq. (1)}$$

where W_n is the weight fraction of hydrocarbons containing n carbon atoms and α is the chain propagation probability, i.e. the probability that a molecule continues reacting to form a longer chain. The α value is obtained by taking the linear slope of $\log (W_n/n)$ and n (the ASF plots can be found in Fig. S5). The α values for CO and CO₂ hydrogenation are identical (see Table 6). Also note that α values for the Fe/Mo₂C and Co/Mo₂C catalysts

Table 6. Chain propagation probabilities for the M/Mo₂C catalysts

Catalysts	Chain propagation probability (α)	
	CO ₂ Hydrogenation	CO Hydrogenation
Mo ₂ C	0.21 ± 0.02	--
Cu/Mo ₂ C	0.22 ± 0.01	0.22 ± 0.02
Pd/Mo ₂ C	0.21 ± 0.02	--
Co/Mo ₂ C	0.27 ± 0.01	--
Fe/Mo ₂ C	0.31 ± 0.02	0.31 ± 0.02

were higher than those for other catalysts for both CO₂ and CO hydrogenation. These results are consistent with literature indicating that Fe and Co are effective for chain propagation during FTS [68, 71], while Cu or Pd produce surface intermediates that lead to C₁ products, i.e. CH₄ and CH₃OH [18, 63, 72]. While CH₃OH was an additional source of CH₄, the contribution was insignificant such that the α values were not affected.

Three mechanisms have been suggested for the formation of C₂₊ products during CO hydrogenation [73, 74]: the carbide, oxygenate, and CO insertion mechanisms. Recently, a mechanistic study performed by Schaidle et al. [75] implicated that the chain

growth over Mo₂C-based catalysts was primarily via the oxygenate mechanism. This mechanism involved the molecular adsorption of CO and subsequent hydrogenation to produce surface methoxy species (–CHO); C-C coupling then occurred via condensation of the –CHO species and hydrogenation steps. This pathway produces alcohols as the side products during the chain growth to form hydrocarbons, which was consistent with ethanol formation at 200 °C for our study. Iron-based catalysts have also been reported to perform chain propagation via the oxygenate mechanism [54]. In fact, Mo₂C-based catalysts are known to dissociatively and associatively adsorb CO, with the latter being responsible for chain propagation [75]. Given our results, we believe the addition of Fe introduced additional associative adsorption sites over Mo₂C, which likely modified Mo₂C and resulted in an enhancement in C₂₊ hydrocarbon formation.

Two pathways have been suggested for CH₃OH production; one involving surface formate and formaldehyde species and the other involving CO as the major intermediate [76-78]. In comparing the CH₃OH production rates during CO and CO₂ hydrogenation, we found that CO contributed insignificantly (3-7%) to the total CH₃OH production, implicating surface formates and aldehydes as principal intermediates. Interestingly, neither formic acid nor aldehyde were detected during the reaction. We believe that these species were rapidly converted, given the thermodynamic favorability (Table S1).

5. Conclusions

In summary, a series of Mo₂C-supported metal catalysts were evaluated for CO₂ hydrogenation at 135-200 °C in 1,4-dioxane solvent. At 135 °C, the catalyst favored CH₃OH with selectivities up to 95%, while at 200 °C, the selectivity shifted to C₂H₅OH (~15%) and C₂-C₄ (5-10%) hydrocarbons with a reduced selectivity to CH₃OH formation (50-70%). A comparison of the product distributions over the M/Mo₂C catalysts revealed that the addition of Cu and Pd enhanced CH₃OH synthesis, while the deposition of Co and Fe enhanced C-C coupling to produce C₂-C₄ hydrocarbons and ethanol. Our analysis of the reaction pathway suggested that CO was the intermediate for hydrocarbon production via FTS, while CO₂ was the primary source for CH₃OH likely via surface formate/aldehyde intermediates. The M/Mo₂C catalysts were robust and experienced minimal changes in catalytic activity and physical/surface properties as a consequence of use for CO₂

hydrogenation. The results also suggested that Mo₂C possessed distinct sites for the production of alcohols and hydrocarbons. The activities of these sites can be altered by, for example, depositing metals or changing the synthesis/treatment protocols. The findings from this study advance our understanding of the low temperature CO₂ hydrogenation activities of carbide supported metal catalysts and provide insights for the design of these types of materials for other reactions.

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References

- [1] J.J. Conti, P.D. Holtberg, J.R. Diefenderfer, S.A. Napolitano, A.M. Schaal, J.T. Turnure, L.D. Westfall, World energy outlook 2015, Energy Information Administration.
- [2] W. Wang, S. Wang, X. Ma, J. Gong, Chem. Soc. Rev. 40 (2011) 3703-3727.
- [3] E.A. Quadrelli, G. Centi, J. Duplan, S. Perathoner, ChemSusChem 4 (2011) 1194-1215.
- [4] G. Centi, E.A. Quadrelli, S. Perathoner, Energy Environ. Sci. 6 (2013) 1711-1731.
- [5] G.A. Olah, G.K.S. Prakash, A. Goepfert, J. Am. Chem. Soc. 133 (2011) 12881-12898.
- [6] M. Aresta, Carbon dioxide as chemical feedstock, John Wiley & Sons, 2010.
- [7] G. Centi, G. Iaquaniello, S. Perathoner, ChemSusChem 4 (2011) 1265-1273.
- [8] D. Aaron, C. Tsouris, Separation Science and Technology 40 (2005) 321-348.
- [9] H. Patrick, Michel Prud'homme, Fertilizer Outlook 2014-2018, International Fertilizer Industry Association.
- [10] M. Aresta, A. Dibenedetto, Dalton Transactions (2007) 2975-2992.
- [11] G.A. Olah, A. Goepfert, G.K.S. Prakash, J. Org. Chem. 74 (2008) 487-498.
- [12] M. Ni, M.K. Leung, D.Y. Leung, K. Sumathy, Renewable and Sustainable Energy Reviews 11 (2007) 401-425.
- [13] H. Sakurai, A. Ueda, T. Kobayashi, M. Haruta, Chem. Commun. (1997) 271-272.
- [14] A. Goguet, F.C. Meunier, D. Tibiletti, J.P. Breen, R. Burch, The Journal of Physical Chemistry B 108 (2004) 20240-20246.

- [15] Z. Kowalczyk, K. Stolecki, W. Rarog-Pilecka, E. Miśkiewicz, E. Wilczkowska, Z. Karpiński, *Appl. Catal.*, A 342 (2008) 35-39.
- [16] G.D. Weatherbee, C.H. Bartholomew, *J. Catal.* 77 (1982) 460-472.
- [17] L. Fan, K. Fujimoto, *Appl. Catal.*, A 106 (1993) L1-L7.
- [18] Y. Yang, J. Evans, J.A. Rodriguez, M.G. White, P. Liu, *Phys. Chem. Chem. Phys.* 12 (2010) 9909-9917.
- [19] C.-S. Chen, W.-H. Cheng, S.-S. Lin, *Catal. Lett.* 68 (2000) 45-48.
- [20] W.C. Conner Jr, J.L. Falconer, *Chem. Rev.* 95 (1995) 759-788.
- [21] S. Oyama, *Catal. Today* 15 (1992) 179-200.
- [22] P.M. Patterson, T.K. Das, B.H. Davis, *Appl. Catal.*, A 251 (2003) 449-455.
- [23] J.J. Patt, *Carbide and Nitride Catalysts for the Water Gas Shift Reaction*, University of Michigan, 2003.
- [24] N.M. Schweitzer, J.A. Schaidle, O.K. Ezekoye, X. Pan, S. Linic, L.T. Thompson, *J. Am. Chem. Soc.* 133 (2011) 2378-2381.
- [25] W. Setthapun, S. Bej, L. Thompson, *Top. Catal.* 49 (2008) 73-80.
- [26] J.-L. Dubois, K. Sayama, H. Arakawa, *Chem. Lett.* 21 (1992) 5-8.
- [27] A.B. Vidal, L. Feria, J. Evans, Y. Takahashi, P. Liu, K. Nakamura, F. Illas, J.A. Rodriguez, *J. Phys. Chem. Lett.* 3 (2012) 2275-2280.
- [28] W. Xu, P. Ramirez, D. Stacchiola, J. Rodriguez, *Catal. Lett.* 144 (2014) 1-7.
- [29] M.D. Porosoff, X. Yang, J.A. Boscoboinik, J.G. Chen, *Angew. Chem.* 126 (2014) 6823-6827.
- [30] L. Fan, Y. Sakaiya, K. Fujimoto, *Appl. Catal.*, A 180 (1999) L11-L13.
- [31] S. Natesakhawat, J.W. Lekse, J.P. Baltrus, P.R. Ohodnicki, B.H. Howard, X. Deng, C. Matranga, *ACS Catal.* 2 (2012) 1667-1676.
- [32] C.A. Huff, M.S. Sanford, *J. Am. Chem. Soc.* 133 (2011) 18122-18125.
- [33] K.K.M. Yu, S.C. Tsang, *Catal. Lett.* 141 (2011) 259-265.
- [34] Y. Chen, S. Choi, L.T. Thompson, *ACS Catal.* 5 (2015) 1717-1725.
- [35] Y. Liu, W. Zhang, T.J. Pinnavaia, *J. Am. Chem. Soc.* 122 (2000) 8791-8792.
- [36] M.J. Verhoef, P.J. Kooyman, J.A. Peters, H. van Bekkum, *Microporous Mesoporous Mater.* 27 (1999) 365-371.
- [37] J.A. Schaidle, N.M. Schweitzer, O.T. Ajenifujah, L.T. Thompson, *J. Catal.* 289 (2012) 210-217.
- [38] B.M. Wyvratt, J.R. Gaudet, L.T. Thompson, *J. Catal.* 330 (2015) 280-287.
- [39] H.P. Klug, L.E. Alexander, *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials*, 2nd ed., Wiley-VCH, 1974.
- [40] E. Brunner, *J. Chem. Eng. Data* 30 (1985) 269-273.
- [41] D. Kassim, H. Zainel, S. Al-Asaf, E. Talib, *Fluid Phase Equilib.* 41 (1988) 287-294.
- [42] J. Evans, M. Wainwright, A. Bridgewater, D. Young, *Appl. Catal.* 7 (1983) 75-83.
- [43] P. Canton, G. Fagherazzi, M. Battagliarin, F. Menegazzo, F. Pinna, N. Pernicone, *Langmuir* 18 (2002) 6530-6535.
- [44] S. Alayoglu, F. Tao, V. Altoe, C. Specht, Z. Zhu, F. Aksoy, D. Butcher, R. Renzas, Z. Liu, G. Somorjai, *Catal. Lett.* 141 (2011) 633-640.
- [45] R.C. Reuel, C.H. Bartholomew, *J. Catal.* 85 (1984) 63-77.
- [46] D. Panayotov, M. Khristova, D. Mehandjiev, *J. Catal.* 156 (1995) 219-228.
- [47] E. Guglielminotti, *The Journal of Physical Chemistry* 98 (1994) 4884-4891.
- [48] P. Dowben, M. Grunze, *Langmuir* 2 (1986) 368-372.
- [49] J.A. Schaidle, *Carbide and Nitride Based Catalysts for Synthesis Gas Conversion*, University of Michigan, 2011.
- [50] M. Saito, R.B. Anderson, *J. Catal.* 67 (1981) 296-302.

- [51] H. Ren, W. Yu, M. Saliccioli, Y. Chen, Y. Huang, K. Xiong, D.G. Vlachos, J.G. Chen, *ChemSusChem* 6 (2013) 798-801.
- [52] Y. Jin, A.K. Datye, *J. Catal.* 196 (2000) 8-17.
- [53] T. Herranz, S. Rojas, F.J. Pérez-Alonso, M. Ojeda, P. Terreros, J.L.G. Fierro, *J. Catal.* 243 (2006) 199-211.
- [54] B.H. Davis, *Catal. Today* 141 (2009) 25-33.
- [55] T.E. King, *Carbide and Nitride Supported Water-Gas Shift Catalysts*, University of Michigan, 2007.
- [56] W. Setthapun, *Carbide and Nitride Supported Methanol Steam Reforming Catalysts*, University of Michigan, 2007.
- [57] S. Srinivas, P.K. Rao, *J. Catal.* 148 (1994) 470-477.
- [58] V.V.e. Rozanov, O.V. Krylov, *Russian chemical reviews* 66 (1997) 107-119.
- [59] K.M.V. Bussche, G.F. Froment, *J. Catal.* 161 (1996) 1-10.
- [60] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R.W. Fischer, J.K. Nørskov, R. Schlögl, *Science* 336 (2012) 893-897.
- [61] I. Kasatkin, P. Kurr, B. Kniep, A. Trunschke, R. Schlögl, *Angew. Chem.* 119 (2007) 7465-7468.
- [62] X. Jiang, N. Koizumi, X. Guo, C. Song, *Applied Catalysis B: Environmental* 170-171 (2015) 173-185.
- [63] T. Fujitani, I. Nakamura, *Bulletin of the Chemical Society of Japan* 75 (2002) 1393-1398.
- [64] S.E. Collins, J.J. Delgado, C. Mira, J.J. Calvino, S. Bernal, D.L. Chiavassa, M.A. Baltanás, A.L. Bonivardi, *J. Catal.* 292 (2012) 90-98.
- [65] C. Schild, A. Wokaun, A. Baiker, *Fresenius' J. Anal. Chem.* 341 (1991) 395-401.
- [66] F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro, F. Frusteri, *J. Catal.* 249 (2007) 185-194.
- [67] G.D. Weatherbee, C.H. Bartholomew, *J. Catal.* 87 (1984) 352-362.
- [68] S. Li, S. Krishnamoorthy, A. Li, G.D. Meitzner, E. Iglesia, *J. Catal.* 206 (2002) 202-217.
- [69] H. Arakawa, A.T. Bell, *Industrial & Engineering Chemistry Process Design and Development* 22 (1983) 97-103.
- [70] T. Riedel, M. Claeys, H. Schulz, G. Schaub, S.-S. Nam, K.-W. Jun, M.-J. Choi, G. Kishan, K.-W. Lee, *Appl. Catal., A* 186 (1999) 201-213.
- [71] D. Schanke, S. Vada, E. Blekkan, A. Hilmen, A. Hoff, A. Holmen, *J. Catal.* 156 (1995) 85-95.
- [72] A.A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov, *Energy Environ. Sci.* 3 (2010) 1311-1315.
- [73] B.H. Davis, *Fuel Process. Technol.* 71 (2001) 157-166.
- [74] G.P. Van Der Laan, A. Beenackers, *Catalysis Reviews* 41 (1999) 255-318.
- [75] J.A. Schaidle, L.T. Thompson, *J. Catal.* 329 (2015) 325-334.
- [76] J. Ye, C.-j. Liu, D. Mei, Q. Ge, *J. Catal.* 317 (2014) 44-53.
- [77] L.C. Grabow, M. Mavrikakis, *ACS Catal.* 1 (2011) 365-384.
- [78] J. Weigel, R.A. Koeppe, A. Baiker, A. Wokaun, *Langmuir* 12 (1996) 5319-5329.

Graphical Abstract