CO_2 hydrogenation: Na Doping Promotes CO and Hydrocarbon Formation Over Ru/m-ZrO_2 at Elevated Pressure

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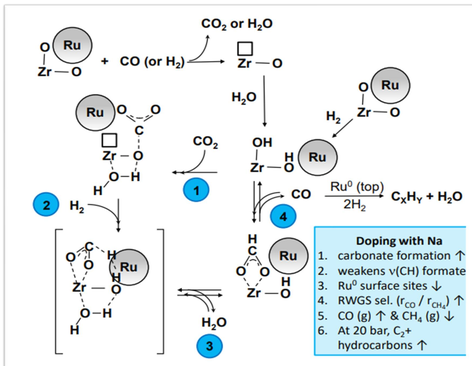

INTRODUCTION

The intention of this research is to design a system that is able to manufacture synthetic fuel, such as diesel, from recycled carbon dioxide. This process was accomplished by using a hybrid catalyst promoted reverse water-gas shift followed by the Fischer-Tropsch synthesis process. The catalyst utilized in this experiment is Ru/m-ZrO_2, a Ruthenium-based catalyst doped with varying quantities of sodium ranging from 1% to 5%. This experiment allows us to observe the effects that the different percentages of sodium (Na) had on the methanation and activation energy, thus changing the overall selectivity. The optimal Na percent at high pressure was found to be approximately 1.8% to 2.5% Na.

Chemical Formulas for Process

Reverse water-gas shift: $CO_2 + H_2 = CO + H_2O$

Fischer-Tropsch synthesis: $CO + 2H_2 = [CH_2]_n + H_2O$

Methanation: $CO + 3H_2 = CH_4 + H_2O$

METHODS

Carbon dioxide (CO_2) from fossil fuels has increased approximately by 90% in the atmosphere ever since 1970. CO_2 emissions negatively impact the climate by increasing global warming. As people continue to rely on natural gas, electricity, and other forms of fossil fuels, CO_2 emissions continue to be released into the air causing climate change. A solution to this problem is CO_2 Hydrogenation where CO_2 undergoes a Reverse water gas shift (RWGS) mechanism to produce CO, followed by either a Fischer Tropsch synthesis (FTS) to convert CO into diesel fuel or methanation as a secondary reaction. In the research, a hybrid Na-doped 1%Ru/m-ZrO2 catalyst at an elevated pressure of 20 bar, 300°C with a space velocity of 80,000 mL/g_{cat}·h , and a H_2/CO_2 ratio of 3:1 was utilized. After RWGS takes place, a secondary reaction of CO occurs on Ru metal on-top sites to produce CH_4. While methanation can be beneficial in creating synthetic natural gas to be used in households, the goal of this research is to produce CO as a reactant for the FTS reaction. The specified elevated pressure of 20 bar suppresses the methanation, which expands the probability of carbon chain growth. One method to control the selectivity of CO is to increase the addition of Na-doping. Increasing the addition of Na can increase surface basicity by strengthening the -CO_2 functional group of formate at the rate-limiting step, while the CH bond of the formate weakens. Na addition also suppresses Ru on-top sites where methanation occurs, decreasing CH_4 selectivity. Thus, increasing Na-doping, helps to control the products of the RWGS reaction by increasing CO selectivity that is later utilized in FTS to produce fuel.

SKILLS & EXPERIANCES

- X-Ray Absorption Near Edge Structure (XANES)
- Extended X-Ray Absorption Fine Structure (EXAFS)
- WinXas Data Processing
- OMNIC Spectroscopy Software
- Technical Writing & Data Analysis

RESULTS

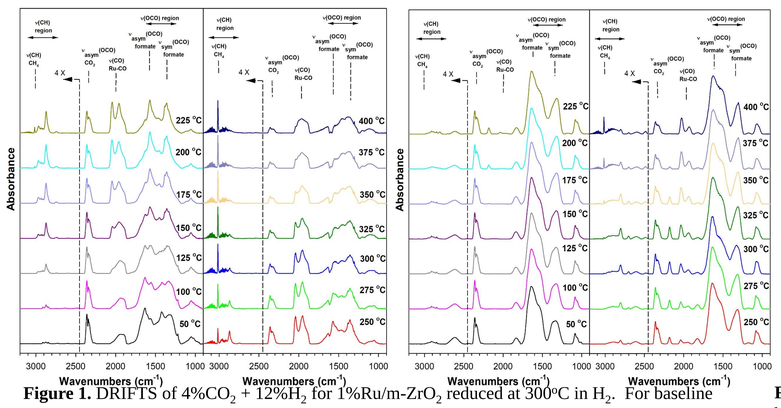

Figure 1. DRIFTS of 4%CO_2 + 12%H_2 for 1%Ru/m-ZrO_2 reduced at 300°C in H_2. For baseline comparison.

Figure 2: DRIFTS of 4%CO_2 + 12%H_2 for 2.5%Na-1%Ru/m-ZrO_2 reduced at 300°C in H_2. Na addition causes the formate C-H band to be shifted to lower wave numbers, the bond weakens which promotes formate formation and CO production, while methanation is suppressed.

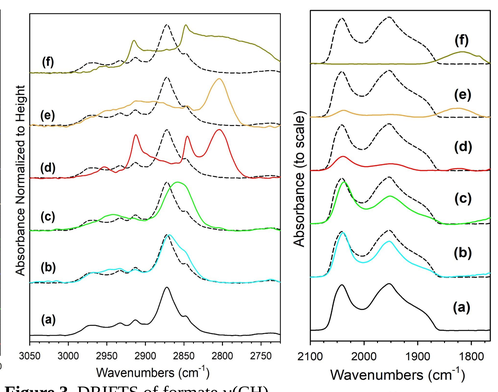

Figure 3. DRIFTS of formate ν(CH) band, during CO_2 hydrogenation using 4%CO_2 + 12%H_2 over catalysts reduced at 300°C. Electronic weakening of formate C-H bond as Na is increased.

Figure 4. Effect of Na on attenuating the Ru carbonyl sites ν(CO) band intensity following CO adsorption at varying temps.

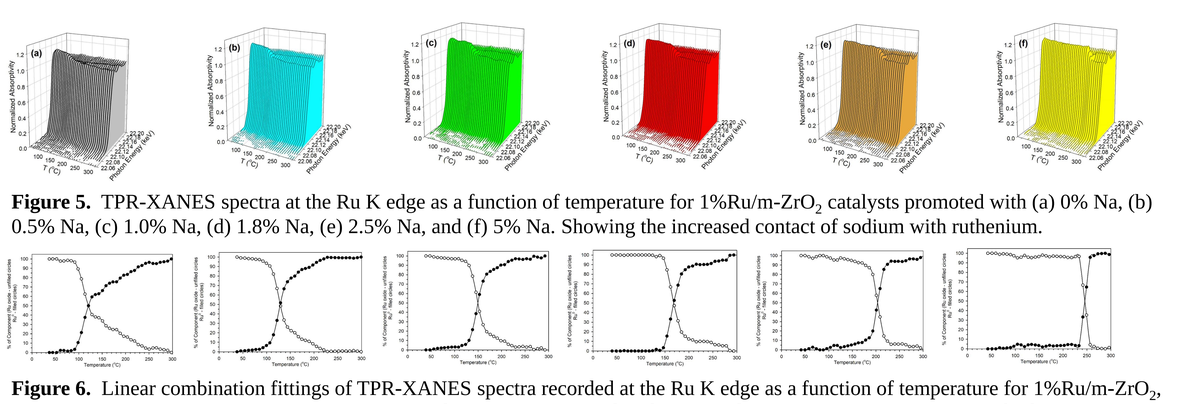

Figure 5. TPR-XANES spectra at the Ru K edge as a function of temperature for 1%Ru/m-ZrO_2 catalysts promoted with (a) 0% Na, (b) 0.5% Na, (c) 1.0% Na, (d) 1.8% Na, (e) 2.5% Na, and (f) 5% Na. Showing the increased contact of sodium with ruthenium.

Figure 6. Linear combination fittings of TPR-XANES spectra recorded at the Ru K edge as a function of temperature for 1%Ru/m-ZrO_2, 0% Na, 0.5% Na, 1.0% Na, 1.8% Na, 2.5% Na, and 5% Na, Respectively. The point of 50% conversion increases to a higher temperature with each increase of Na percent, this indicates direct contact between Na and Ru.

Sample Description	N Ru-Ru metal	Est. # atoms	Est. Diam. (nm)
Ru^0 foil	**12**	-	-
0%Na-1%Ru/m-ZrO_2	2.0 (0.81)	4.7	0.31
0.5%Na-1%Ru/m-ZrO_2	3.7 (0.47)	8.6	0.56
1%Na-1%Ru/m-ZrO_2	3.4 (0.42)	7.9	0.52
1.8%Na-1%Ru/m-ZrO_2	3.1 (0.64)	7.2	0.47
2.5%Na-1%Ru/m-ZrO_2	3.7 (0.72)	8.7	0.57
5%Na-1%Ru/m-ZrO_2	4.5 (0.32)	10.6	0.69

Table 1. EXAFS fittings for Ru K-edge data and the size estimations.

1% Ru/ZrO_2 - 2.5% Na vs. 5% Na – 80,000 mL/g cat/hr 300° C, 20 bar, 2 hr. H_2:CO_2 3:1

	1% Ru/ZrO_2, 2.5% Na Converted	1% Ru/ZrO_2, 5% Na Converted
CO Selectivity	36%	71%
CH_4 Selectivity	60%	21%
C_2-C_4 Selectivity	4%	8%
CO_2 Selectivity	14%	10%

Table 2. Selectivity results of reaction testing in a fixed bed reactor. The results show an impressive increase in CO selectivity and a remarkable decrease in undesired CH4 selectivity.

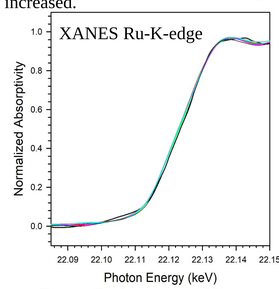

Figure 7. Overlays of H_2 reduced catalysts. No evidence for electron charge transfer from Na to Ru.

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