Na-Doping Promotes CO and Hydrocarbon Formation over Ru/m-ZrO_2 during CO_2 Hydrogenation at 20 Bar

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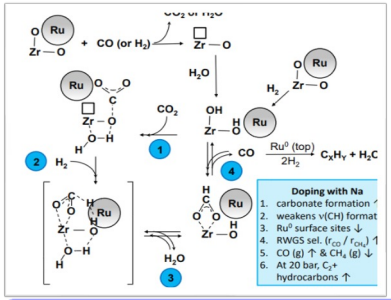
INTRODUCTION

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 involving a hybrid catalyst promoted by reverse water-gas shift followed by the Fisher-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 of different sodium (Na) percentages on the methanation and activation energy, thus effecting and controlling 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: $CO_2 + H_2 = CO + H_2O$
Fisher-Tropsch synthesis: $CO + 2H_2 = [CH_2]_n + H_2O$
Methanation: $CO + 3H_2 = CH_4 + H_2O$



METHODS

CO_2 from fossil fuels has increased approximately by 90% in the atmosphere ever since 1970, which negatively impacts the climate by increasing global warming. As people continue to rely on fossil fuels, more CO_2 emissions are released into the air. A solution to this is facilitating a hybrid Na-doped 1%Ru/m-ZrO_2 catalyst consisting of reverse water-gas shift (RWGS) and Fisher-Tropsch synthesis functions being tested at 20 bar, 300ºC, SV of 80,000 mL/gcat·h, and H_2/CO_2 = 3:1. During the RWGS process, a secondary reaction of CO takes place where CH_4 is produced on Ru metal on-top sites. The addition of Na plays an important role in mitigating this undesired reaction. Although increasing Na-doping from 2.5%Na to 5%Na slightly decreased CO_2 conversion from 14% to 10%, selectivity was remarkably improved. CH_4 selectivity decreased from 60% to 21%, while CO selectivity virtually doubled from 36% to 71%. Infrared spectroscopy experiments at 1 atm and H_2/CO_2 = 3:1 showed that the addition of Na increases surface basicity and attenuates Ru activity. The increased basicity promotes the adsorption of CO_2, weakens the formate CH bond increasing CO selectivity during RWGS, and hinders methanation on Ru on-top sites. At 20 bar, the suppression of methanation allows the probability for carbon chain growth to be enhanced. A decrease in the reduction rate during TPR and TPR-EXAFS/XANES at the Ru K-edge suggests that Na is in direct contact with Ru. Following H_2 reduction, all catalysts displayed spectra of reduced Ru metal; there was no significant alteration of the white line intensity, suggesting that electronic modification of the catalyst is not due to charge transfer, but rather an effect of enhanced basicity by Na addition. Higher surface basicity increases the bond strength between the catalyst surface and the -CO_2 functional group of formate, resulting in the weakening of the formate C-H bond.

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

Reverse water-gas shift: $CO_2 + H_2 = CO + H_2O$
Fisher-Tropsch synthesis: $CO + 2H_2 = [CH_2]_n + H_2O$
Methanation: $CO + 3H_2 = CH_4 + H_2O$

RESULTS

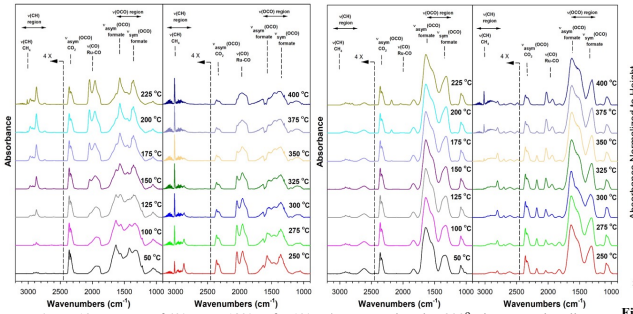


Figure 12. DRIFTS of 4%CO_2 + 12%H_2 for 1%Ru/m-ZrO_2 reduced at 300ºC in H_2. For baseline comparison.

Figure 16: DRIFTS of 4%CO_2 + 12%H_2 for 2.5%Na-1%Ru/m-ZrO_2 reduced at 300ºC in H_2. It can be observed that the methanation has been suppressed and formate shifts to lower wave

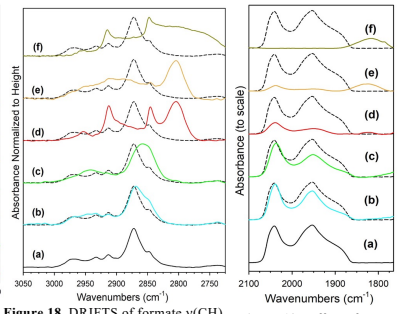


Figure 18. DRIFTS of formate ν(CH) band, during CO_2 hydrogenation using 4%CO_2 + 12%H_2 over catalysts reduced at 300ºC. Electronic weakening of formate as Na is increased.

Figure 10. Effect of Na on attenuating the Ru carbonyl sites ν(CO) band intensity following CO adsorption at varying temps.

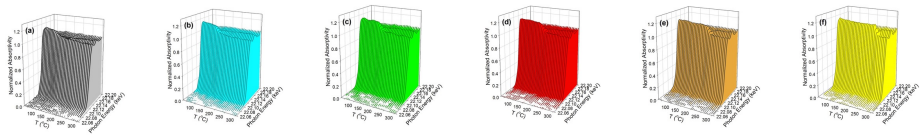


Figure 3. TPR-XANES spectra at the Ru K edge as a function of temperature for 1%Ru/m-ZrO_2 catalysts promoted with (a) 0% Na, (b) 0.5% Na, (c) 1.0% Na, (d) 1.8% Na, (e) 2.5% Na, and (f) 5% Na. Showing the increased contact of sodium with ruthenium.

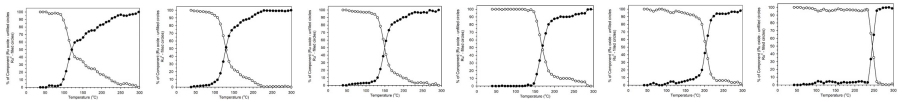


Figure 4. Linear combination fittings of TPR-XANES spectra recorded at the Ru K edge as a function of temperature for 1%Ru/m-ZrO_2, 0% Na, 0.5% Na, 1.0% Na, 1.8% Na, 2.5% Na, and 5% Na, Respectively. The point of 50% conversion increases to a higher temperature with each increase of Na percent. This indicates direct contact between Na and Ru.

1% Ru/ZrO_2 - 2.5% Na vs. 5% Na – 80,000 mL/g cat/hr 300º 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 1. Selectivity results of reaction testing in a fixed bed reactor. The results show an impressive increase in CO selectivity and remarkable decrease in undesired CH_4 selectivity.

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

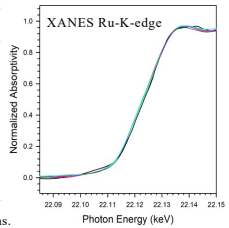


Figure 34. Overlays of H_2 reduced catalysts. No evidence for electron charge transfer from Na to Ru.

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