CO_2 Hydrogenation on Na-Doped Ruthenium Zirconia Catalysts

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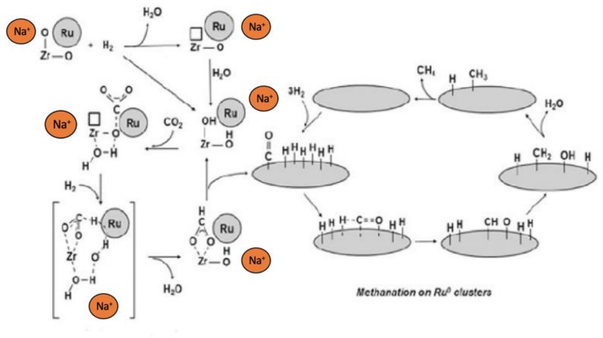
Heterogenous Catalysis

Heterogenous Catalysis involves a catalyst in a phase that is different from that of the reactants. This differs from homogeneous catalysis, where reactants are in the same phase as the catalyst. Catalysts are essential since they control selectivity and allow reactions to occur faster by lowering the activation energy. The selectivity of catalysts involves the ability to direct a reaction toward a specific product, and here the aim was to control the selectivity of CO_2 hydrogenation catalysts to produce either CO or CH_4 products. CO can be further reacted to produce diesel and jet fuels by Fischer-Tropsch synthesis, while CH_4 can be used as synthetic natural gas for home heating. Dr. Jacobs and Caleb Watson prepared Na-doped Ru/ZrO_2 catalysts for CO_2 hydrogenation, which were characterized by them and Martin Ayala using a variety of techniques at UTSA such as infrared spectroscopy. The catalysts were then sent to Argonne National Laboratory to be run at the Advanced Photon Source. My contribution was focused on analyzing the vast synchrotron data to determine: (1) using x-ray absorption near edge spectroscopy (XANES) whether Na electronically modifies the structure of ruthenium and (2) assess Ru particle size using extended x-ray absorption fine structure spectroscopy (EXAFS).

Background

Mechanism for Water-Gas Shift & Methanation



Carbon dioxide (CO_2) emissions in the air have increased from 22 to 33 billion metric tons between 1990 and 2015. CO_2 emissions is one of the leading causes of global warming. As populations consume more energy, more CO_2 is emitted to the atmosphere. For example, as coal plants produce electricity for human consumption a byproduct is CO_2. A solution to this problem is CO_2 hydrogenation via reverse water gas shift (RWGS) producing CO, followed by either Fischer-Tropsch synthesis (FTS) to make diesel and jet fuels or methanation. In the current investigation conducted at low pressure, the goal was to control the selectivity of Ru/m-ZrO_2 catalysts by controlling the relative rates of RWGS and methanation through Na doping. At high RWGS/methanation ratios, the aim is to produce CO, which would be sent downstream to a higher pressure (~20 bar) FTS reactor where the CO would be reacted with $2H_2$ to produce hydrocarbon fuels. At high methanation/RWGS rates, the CO is intercepted and converted to methane on the catalyst directly at low pressure. Methane can be used as synthetic natural gas for home heating. There are two reasons for adding Na to the catalyst. First, Na addition increases the RWGS rate by weakening the formate C-H bond and accelerating CH bond formation of the formate intermediate. This is the proposed rate limiting step of the RWGS mechanism, which occurs at the junction between the Ru particles and defects in the ZrO_2 support. Second, Na tends to block Ru sites on top of the Ru particles, where methanation occurs. As such, methanation is expected to be inhibited. Thus, by increasing the Na loading, we expect to see a higher selectivity to CO and a lower selectivity to CH_4. This is beneficial if we want to send the CO downstream to be converted by Fischer-Tropsch synthesis (using a higher pressure reactor) to hydrocarbon fuels.

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

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

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

Objectives

- Examine the impact of Na on the electronic structure of Ru/ZrO_2 catalysts
- Analyze synchrotron data via EXAFS and XANES
- Determine the average Ru^0 diameter of the catalysts

Results

Table 1: Catalyst testing using a fixed bed reactor: P = 1 atm, T= 300°C; H_2/CO_2 = 4.

Catalysts	CO_2 conversion (%)	Reaction rates ($mol/mol_{Ru}.s$)	CH_4 selectivity (%)	CO selectivity (%)
Ru/ZrO_2	6.5	1.10	97	3
$Ru/0.5Na\text{-}ZrO_2$	9.5	0.42	96	4
$Ru/1.0Na\text{-}ZrO_2$	5.7	0.25	88	12
$Ru/1.8Na\text{-}ZrO_2$	4.4	0.20	41	59
$Ru/2.5Na\text{-}ZrO_2$	4.8	0.13	41	59
$Ru/5.0Na\text{-}ZrO_2$	5.2	0.08	19	81

1% Ru/ZrO_2 had a high selectivity for CH_4. The experimental data demonstrates the incrementation of Na loadings to the catalysts. As more Na is added selectivity shifts to CO, as expected.

1. (Na) $CO_2 + H_2 \rightarrow CO + H_2O$
2. (Ru) $CO + 3H_2 \rightarrow CH_4 + H_2O$

Na addition speeds up the first reaction and hinders the 2nd reaction by blocking ruthenium sites.

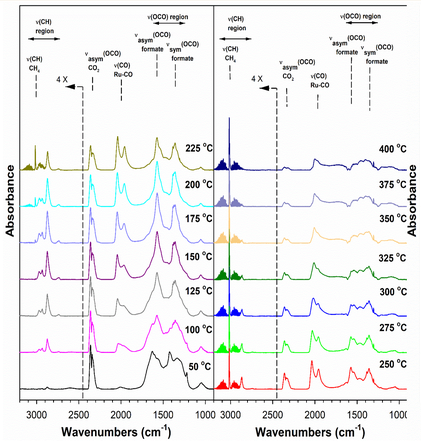


Figure 1: DRIFTS of CO_2 + H_2 for 1%Ru/ZrO_2 reduced at 300°C in H_2. Methane already starts to form at 200°C. Formate ν(CH) band at 2870 cm^{-1}.

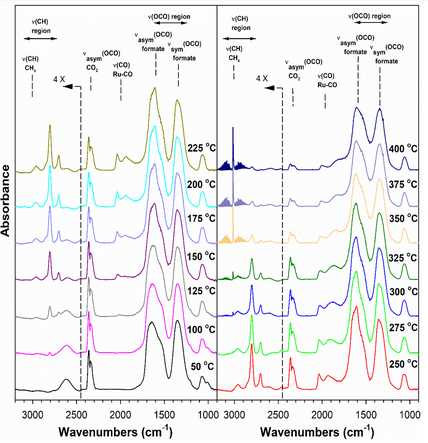
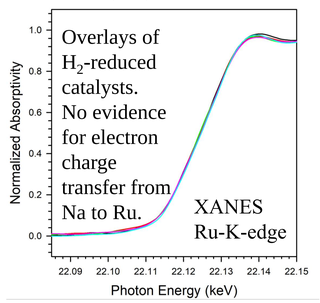


Figure 2: DRIFTS of CO_2 + H_2 for 2.5%Na-1%Ru/ZrO_2 reduced at 300°C in H_2. Methane begins to form at 325°C. Na dopant inhibits methane formation, as expected. Formate ν(CH) band at 2806 cm^{-1}. Formate C-H bond is weakened in presence of Na. Ru carbonyl bands at ~2000 cm^{-1} are suppressed indicating blocking of Ru^0 surface sites by Na, suppressing Ru^0-catalyzed methanation.



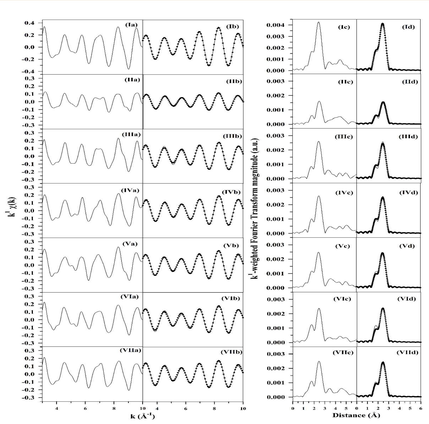


Figure 3: EXAFS fittings for data recorded near the Ru K-edge, including (a) raw k^1-weighted c(k) data, (b) (solid line) filtered k^1-weighted c(k) data and (filled circles) results of the fittings, (c) raw and (d) filtered k^1-weighted Fourier transform magnitude (solid line) data and (filled circles) results of the fittings for (I) Ru^0 foil, (II) 1%$Ru/m\text{-}ZrO_2$, and 1%$Ru/m\text{-}ZrO_2$ with (III) 0.5%Na, (IV) 1%Na, (V) 1.5%Na (VI) 2.5%Na and (VII) 5%Na.

Table 2: Table demonstrating the results of EXAFS fittings. The average Ru diameter was 0.67 nm.

Sample Description	N Ru-Ru metal	R Ru-Ru (Å) Metal	e_0 (eV)	σ^2 (Å²)	r-factor	Est. # atoms *	Est. Diam. (nm) *
Ru^0 foil	**12 (6 + 6) (fixed)**	2.664 (0.0437) 2.676 (0.0415)	3.85 (2.28) -7.61 (2.30)	0.00286 (0.00222)	0.0069	-	-
0%Na-1%Ru/m-ZrO_2	3.1 (0.40)	2.684 (0.0064)	0.968 (0.865)	0.00163 (0.00106)	0.013	8.0	0.70
0.5%Na-1%Ru/m-ZrO_2	4.7 (0.63)	2.663 (0.0060)	-1.41 (0.911)	0.00149 (0.00108)	0.013	4.4	0.57
1%Na-1%Ru/m-ZrO_2	4.4 (0.57)	2.668 (0.0060)	0.223 (0.880)	0.00052 (0.00102)	0.012	7.2	0.67
1.5%Na-1%Ru/m-ZrO_2	4.3 (0.49)	2.669 (0.0053)	-1.12 (0.779)	0.00059 (0.00089)	0.0088	6.9	0.66
2.5%Na-1%Ru/m-ZrO_2	4.5 (0.70)	2.664 (0.0075)	-1.33 (1.07)	0.00123 (0.00126)	0.017	7.5	0.68
5%Na-1%Ru/m-ZrO_2	4.8 (0.77)	2.669 (0.0079)	-0.663 (1.09)	0.00170 (0.00132)	0.019	8.3	0.71

Skills and Experience

- Data Analysis
- WinXas and Excel data processing
- Extended X-Ray Absorption Fine Structure (EXAFS)
- X-Ray Absorption Near Edge Structure (XANES)

Future Plans

In the future with the assistance of South West Research Institute, the plan is to run a reactor with reverse water gas shift and Fischer-Tropsch occurring at a pressure of 20 atm. Running this process at 20 atm should create longer hydrocarbon chains, useful for fuels.

What I learned

I learned that adding Na to the reverse water gas shift reaction will block ruthenium sites. Therefore, adding Na to the catalyst will alter the selectivity of the reaction from CH_4 to CO. This is a very important discovery since the CO produced could eventually be used to run Fisher-Tropsch in the future.

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References

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