ATTRITION RESISTANT FISCHER-TROPSCH CATALYSTS BASED ON SPENT FCC SUPPORTS

S. K. Vasireddy[1], A. A. Adeyiga[2], E. Miamee[2], A. Campos[1], J. J. Spivey[1], J. G. Goodwin, Jr.[3]

[1]Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803
[2]Department of Chemical Engineering, Hampton University, Hampton, VA 23668
Department of Chemical Engineering, Clemson University, Clemson, SC 29634-0909

Introduction

- Relatively low cost, high water gas shift activity and low methane selectivity makes Fe catalysts more preferred for F-T process using syngas derived from coal and biomass.
- Spent FCC catalysts are being used as catalyst supports in this project to address several issues with the FT reaction: attrition and cost effectiveness.
- Two main questions to be answered with this research are: 1) whether iron can be loaded on the catalyst and have appreciable activity 2) whether the loaded iron retains the attrition resistant behavior of the spent FCC catalysts. These two questions are the basis of this research.

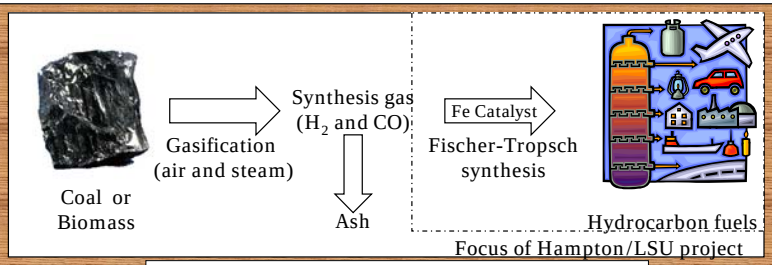


Figure 1 – Conversion of coal/biomass to Fischer-Tropsch fuels

Why consider FCC catalysts as support?

	Spent	Fresh
Cost ($/lb)	0.075-0.34	0.75-1.50
Size distribution (μm)	40-150	40-150
Fines (% <40μm)	Negligible	30
BET surface area	50-175	>300
5 hour attrition loss (%)	0.4	2.6
20 hour attrition loss (%)	1.2	8.0

Table 1– Comparison between fresh FCC catalysts and spent FCC catalysts

BET S.A. results

Catalyst	BET S.A. (m^2 g cat^{-1})
Engelhard-A	101
Engelhard-B	152
Engelhard-C	153
Engelhard-D	137
Engelhard-E	86
Albemarle	158
5 wt% Fe-Albemarle	158
10 wt% Fe-Albemarle	143
15 wt% Fe-Albemarle	148
20 wt% Fe-Albemarle	113
100Fe-5Cu-4.2K/25Engelhard	37
100Fe-5Cu-4.2K/25Albemarle	36

Table 2 – BET surface area results for spent FCC catalysts

Reaction results

15 % Fe supported on spent FCC catalyst (unpromoted)	
% CO conversion	23.6
Hydrocarbon product distribution, wt. percentages	
C_1	20.6
C_2-C_4	53.2
C_5+	26.2

Table 4 – Fixed bed reactor results, T=250°C, 1MPa, H_2/CO=1, WHSV=0.77h^{-1}

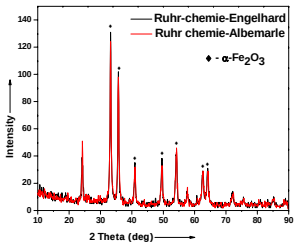
Results and Discussion

- Surface areas were within 50% for all spent FCC materials tested, with Albemarle and Engelhard-C with the highest surface areas
- ICP/MS results show similar composition for different spent FCC materials and most spent FCC catalysts had a Si:Al ratio of 1.15
- Higher Fe loadings (>20%) yield lower BET surface areas, this is due to the pores being filled during the catalyst preparation

Catalyst synthesis

- Spent FCC catalysts were procured commercially from Engelhard and Albemarle corporation.
- Based on the characterization results , best spent FCC catalysts were chosen to use as supports for synthesizing Fe based catalysts
- Fe with and without promoters (Cu & K) were loaded on to the spent FCC supports using incipient impregnation method.
- Ruhr-Chemie catalyst composition was taken as base line in synthesizing the catalysts.

XRD results of calcined catalysts



ICP-MS analysis results

	Albemarle	Engelhard-A	Engelhard-B	Engelhard-C	Engelhard-D	Engelhard-E	100Fe-5Cu-4.2K/25Engelhard	100Fe-5Cu-4.2K/25Albemarle
Al	22.05	20.68	20.6	21.3	16.9	20.7	5.78	5.48
Ca	0.039	0.023	0.34	0.18	0.35	0.13	0.024	0.017
Fe	0.54	0.58	1.25	0.75	0.69	1.1	45.1	44.3
Ni	0.025	0.051	0.013	0.05	0.003	0.092	0.008	0.015
Pt	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Si	21.87	23.89	23.78	24.16	29.36	23.82	5.48	6.27
Ti	0.71	0.7	0.85	0.88	0.34	0.84	0.22	0.23
V	0.081	0.084	0.084	0.17	0.027	0.24	<0.05	<0.05
Zn	0.23	0.009	0.009	0.008	0.003	0.031	0.064	0.003
Zr	0.008	0.018	0.005	0.008	0.004	0.004	0.001	0.002
Cu	-	-	-	-	-	-	1.95	1.92
K	-	-	-	-	-	-	1.26	1.31
Si:Al	0.99	1.16	1.15	1.13	1.74	1.15	0.948	1.14

Table 3 – ICP/MS results (in ppwt.) for spent FCC catalysts

Conclusions

- Iron catalyst on spent FCC material showed moderate FT activity (250°C, 1 MPa, H2:CO=1), which is a proof of concept
- Albemarle and Engelhard-C are a good spent FCC candidate as a support due to higher surface areas as well as similarities in composition and BET surface areas

Future work

- Testing the attrition resistance of the K & Cu promoted Fe based spent FCC supported catalysts
- Evaluating the catalysts activity for F-T synthesis in a fixed bed reactor

Acknowledgements

We would like to thank the HBCU/UCR program within the DOE (DE-FG26-06NT42744), for funding this project, with the industrial collaboration with Süd-Chemie Inc. We would also like to thank Adefemi Egbebi and Stefan Ahl for their help with chemisorption and BET experiments, respectively.