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THE ECONOMICAL PRODUCTION OF ALCOHOL FUELS FROM COAL-DERIVED SYNTHESIS GAS

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Executive Summary

During this time period, we finished our data collection for the kinetic study on the reduced Mo-Ni-K/C catalyst. Consequently, we have started the development of the kinetic models, and have obtained some preliminary results. We have also obtained some interesting results in the quantitative analyses of the TPR spectra.

1.1 Introduction

The objective of Task 1 is to prepare and evaluate catalysts and to develop efficient reactor systems for the selective conversion of hydrogen-lean synthesis gas to alcohol fuel extenders and octane enhancers.

Task 1 is subdivided into three separate subtasks: laboratory and equipment setup; catalysis research; and reaction engineering and modeling. Research at West Virginia University (WVU) is focused on molybdenum-based catalysts for higher alcohol synthesis (HAS). Parallel research carried out at Union Carbide Corporation (UCC) was focused on transition-metal-oxide catalysts. This research has been completed and is not reported on here.

1.2 Accomplishments, Results and Discussion

1.2.1 Laboratory Setup

During this reporting period, the equipment for the kinetic study on the reduced Mo-Ni-K/C catalyst and the equipment for the temperature-programmed reduction (TPR) on C-supported Mo-based catalysts have been running well. We are continuing our kinetic study of the Mo-Ni-K/C catalyst and the quantitative analyses of TPR spectra of the components of the catalyst.

1.2.2 Molybdenum-Based Catalyst Research

At WVU, we have finished our data collection for the kinetic study on the reduced Mo-Ni-K/C catalyst. The experimental data were obtained on a tubular fixed-bed microreactor. Similar to the case of the sulfide catalyst, we decided first to develop exponential models to determine the statistically significant variables for each model, and then to develop the final models which include only the statistically significant variables and which are of Langmuir-Hinshelwood (L-H) type for the gross production rates of significant alcohols and total hydrocarbons.

Table 1 shows the reaction temperature and pressure, along with the inlet flow rates and inlet partial pressures, for each experimental point. Note that N_2 was premixed with CO as an internal standard. The average production rates, outlet molar flow rates and outlet partial pressures have been calculated for data points between 15h and 25h of reaction time, and are given in Tables 2 to 4. The molar flow rates of H_2 and H_2O in Table 3 were calculated by balancing hydrogen atoms and by assuming that water-gas-shift (WGS) reaction reaches equilibrium in every case.

Since we have been using a very small amount of catalyst (0.2g), it is reasonable to assume that the product formation rates do not change along the catalyst bed, and are equal to the overall product formation rates as tabulated in Table 2. The calculated gas linear velocity under the central point conditions is 0.7415 cm/min. We consider this to be low enough to assume that the flow pattern is back-mixing, rather than plug flow, although this may be modified later. Therefore, at least initially, it is reasonable to use the arithmetic mean of the inlet and outlet concentrations for the development of the kinetic models for the preliminary interest. Table 5 lists these arithmetic means of inlet and outlet partial pressures.

Similar to the case of the sulfide catalyst, exponential models will first be developed to determine the statistically significant variables for each model. Those variables determined to be statistically insignificant in the exponential models will be dropped off from the final models to be developed.

We report here the development of the exponential models for methanol (MeOH) and ethanol (EtOH). The concept of "gross" production rates was adopted for the development of the model used earlier for the sulfided Mo-Co-K/C catalyst (see MS60), and this is continued here. A nonlinear regression procedure provided in SigmaPlot® was used to fit the exponential models. The F-statistic was used to test the significance of the models, while the significance of the parameter estimates was tested using the t-statistic.

The independent variables considered for MeOH production rate were the reaction temperature, the partial pressures of CO, H_2 and MeOH. The expression for the gross production rate of MeOH can be written as:

$$r_{g,MeOH}=A_1\exp[-(E_1/R)(1/T-1/T_{cp})](P_{CO}/P_{CO,cp})^{a1}(P_{H2}/P_{H2,cp})^{b1}(P_{MeOH}/P_{MeOH,cp})^{c1} \quad (1)$$

The regression results in the following values of parameters:

A_1=19.5 mol/h/kg-cat. (2a)
E_1=46.7 KJ/mol (2b)
a_1=0.237 (dimensionless) (2c)
b_1=0.117 (dimensionless) (2d)
c_1=0.271 (dimensionless) (2e)

The comparison of the experimental and predicted gross production rates for MeOH is shown in Figure 1. The relatively large value of F-statistic (=41.30) and high coefficient of determination (=0.965) indicate the high significance of the model. The value of the t-statistic is greater than 3 for all parameters in Equation (2), indicating that every term in Equation (1) is statistically significant.

Similarly, the expression for the gross production rate of EtOH was initially written as:

$$r_{g,EtOH}=A_2\exp[-(E_2/R)(1/T-1/T_{cp})](P_{CO}/P_{CO,cp})^{a2}(P_{H2}/P_{H2,cp})^{b2}(P_{MeOH}/P_{MeOH,cp})^{c2} \quad (3)$$

The regression gives the following values of parameters:

A_2=11.12 mol/h/kg-cat. (4a)
E_2=85.91 KJ/mol (4b)
a_2=0.3104 (dimensionless) (4c)
b_2=0.5496 (dimensionless) (4d)
c_2=0.3453 (dimensionless) (4e)

The comparison of the experimental and predicted gross production rates for EtOH is shown in Figure 2. The relatively large value of F-statistic (=60.27) and high coefficient of determination (=0.9757) indicate the high significance of the model of Equation (3). But the values of the t-statistic show that none of the terms of Equation (4) is statistically significant, except the pre-exponential and the temperature terms. Hence, alternative models were developed by dropping one term of Equation (3) at a time. When the MeOH-dependency term (c_2) is dropped from the model, both CO and H_2 terms are significant. However, when the CO-dependency term (a_2) is dropped, the H_2-dependency term (b_2) is insignificant while the MeOH-dependency term is significant. Finally, when the H_2 term is dropped, the MeOH term is still significant while CO term is insignificant. This may indicate that only the MeOH term is statistically significant for the model.

We are continuing to analyze quantitatively the TPR spectra for C-supported Mo-based catalysts. The analyses indicate the presence of two low-temperature peaks and one high-temperature peak corresponding to the reduction of Mo species, in addition to a peak for the reduction of carbon support. For Mo/C catalysts (without K- and Ni-doping), varying the Mo loading changes not only the total amount of Mo in the catalyst but also the distribution of different Mo species as well. Increasing the Mo loading results in a larger portion of Mo species that is reducible only at high-temperature.

In the last report (MS66), we presented some TPR raw data for Mo-K/C catalysts. The data can be manipulated as shown in Figure 3. The ratio of the area of the high-temperature peak to that of the total low-temperature peaks decreases substantially with the addition of K into the Mo/C catalyst. With further increasing of K-doping level, the ratio still decreases, but much less rapidly. That means the distribution of different Mo species changes dramatically with the incorporation of K into the catalyst. The amount of Mo species reducible only at high temperature significantly decreases with the initial addition of K. Accordingly, the amount of Mo species reducible at low temperature increases.

The trend can also be seen from the Mo valence present after reduction. For Mo/C catalyst without K, the Mo valence after low temperature reduction is about +5 (assuming the initial Mo oxidation state to be +6). With the addition of K into the catalyst, the Mo valence after low-temperature reduction decreases to around +3, and stays roughly the same with further increasing of K-doping level. On the other hand, the Mo valence after high-temperature reduction is about +2.5 for Mo/C catalyst without K, and decreases by nearly +1 with the initial doping of K. But with further increasing K-doping level, the Mo valence after high-temperature reduction goes up, and then stays almost constant after K/Mo ratio exceeds 1.0.

From these results, we can see that the extent of reduction of Mo at low temperature is greatly enhanced by the incorporation of K into the catalyst. That is to say, at low temperature, Mo can be more easily reduced for catalysts with K than those without K.

1.3 Conclusions and Recommendations

The kinetic data for a Mo-Ni-K/C catalyst were completed. Kinetic schemes were derived for the formation of methanol and ethanol over this catalyst. TPR results on alkali-substituted Mo/C are beginning to be amenable to a systematic quantitative analysis.

1.4 Future Plans

We plan to continue the TPR experiments on alkali-substituted carbon-supported Mo-based catalysts, as well as the qualitative and quantitative analyses of the spectra. We are also continuing our kinetic studies on the reduced Mo-Ni-K/C catalysts.

Table 1. Reaction Conditions and Inlet Feed Composition

Experiment Label	T (K)	Total pressure (psi)	Inlet flow rates (cc STP/min)			Inlet partial pressures (atm)		
			CO	H_2	N_2	CO	H_2	N_2
A	643	800	19.2	30	0.8	20.90	32.65	0.8710
B	643	950	24.0	25	1.0	31.02	32.31	1.293
C	613	800	28.8	20	1.2	31.35	21.77	1.307
D	643	650	24.0	25	1.0	21.22	22.11	0.8846
E	613	650	24.0	25	1.0	21.20	22.11	0.9059
F	643	800	28.8	20	1.2	31.35	21.77	1.307
G	613	800	19.2	30	0.8	20.90	32.65	0.8710
H	613	950	24.0	25	1.0	31.02	32.31	1.293
CP*	628	800	24.0	25	1.0	26.12	27.21	1.089
R-H	613	950	24.0	25	1.0	30.99	32.31	1.324
R-CP*	628	800	24.0	25	1.0	26.10	27.21	1.115

* CP denotes center-point values

Table 2. Average Product Formation Rates during Reaction Time of 15h and 25h

Experiment Label	R-CO_2	R-HC	R-MeOH	R-EtOH	R-PrOH	R-BuOH	R-PenOH	R-HexOH	R-HeptOH	R-T.Alco.
					(g/h/kg-cat.)					
A	2065.23	69.98	103.80	368.48	298.55	146.98	58.65	17.17	4.63	998.20
B	2490.00	98.92	120.85	429.70	406.50	181.45	61.45	15.50	3.38	1218.83
C	1630.38	115.18	82.65	149.07	103.40	60.28	36.38	18.00	8.90	458.63
D	1681.03	183.52	70.73	211.82	155.45	94.57	56.63	24.72	14.83	628.73
E	807.90	165.85	77.57	108.77	79.43	54.70	45.53	33.93	15.25	415.22
F	2031.22	182.55	81.08	239.03	237.27	148.28	78.05	33.82	15.68	833.18
G	980.78	80.05	150.35	187.50	105.50	50.97	30.02	16.48	9.82	550.63
H	1319.45	120.42	167.93	224.72	153.27	79.90	45.73	22.57	11.47	705.57
CP*	1604.53	111.58	130.77	289.30	229.08	107.50	46.38	17.75	7.40	828.17
R-H	1356.98	120.47	155.10	245.87	182.03	74.35	30.35	11.58	4.57	703.88
R-CP*	1534.93	118.75	145.13	281.17	200.98	92.40	39.20	15.73	4.73	779.30

* CP denotes center-point values

Table 3. Average Outlet Molar Flow Rates between Reaction Time of 15h and 25h

Experiment Label	CO	H_2	H_2O	CO_2	N_2	HC	MeOH	EtOH	PrOH	BuOH	PenOH	HexOH	HeptOH
							(mol/h)						
A	0.031618	0.064465	0.00122	0.009453	0.002144	0.00094	0.000653	0.001613	0.001002	0.0004	0.000134	3.39E-05	8.04E-06
B	0.04005	0.047922	0.000862	0.011392	0.002679	0.001327	0.00076	0.00188	0.001364	0.000494	0.000141	3.06E-05	5.88E-06
C	0.063882	0.044945	0.000233	0.007459	0.003215	0.001546	0.00052	0.000652	0.000347	0.000164	8.32E-05	3.55E-05	1.54E-05
D	0.048127	0.05436	0.000549	0.007687	0.002679	0.002462	0.000445	0.000926	0.000521	0.000257	0.00013	4.87E-05	2.57E-05
E	0.054362	0.057937	0.000175	0.003695	0.002744	0.002224	0.000488	0.000476	0.000266	0.000149	0.000104	6.69E-05	2.64E-05
F	0.057322	0.038397	0.000394	0.009288	0.003215	0.002449	0.00051	0.001045	0.000796	0.000403	0.000178	6.67E-05	2.72E-05
G	0.04101	0.071165	0.000345	0.004485	0.002144	0.001074	0.000945	0.00082	0.000354	0.000139	6.86E-05	3.25E-05	1.71E-05
H	0.04101	0.071165	0.000345	0.004485	0.002144	0.001074	0.000945	0.00082	0.000354	0.000139	6.86E-05	3.25E-05	1.71E-05
CP*	0.047788	0.05332	0.000436	0.007341	0.002679	0.001498	0.000823	0.001266	0.000769	0.000292	0.000106	3.5E-05	1.29E-05
R-H	0.050085	0.054963	0.000302	0.006208	0.002744	0.001616	0.000976	0.001076	0.000611	0.000202	6.94E-05	2.29E-05	7.94E-06
R-CP*	0.04852	0.053875	0.000415	0.007019	0.002744	0.001593	0.000912	0.00123	0.000674	0.000251	8.96E-05	3.1E-05	8.19E-06

* CP denotes center-point values

Table 4. Average Outlet Partial Pressures during Reaction Time of 15h and 25h

Experiment Label	CO	H_2	H_2O	CO_2	N_2	HC	MeOH	EtOH	PrOH	BuOH	PenOH	HexOH	HeptOH
							(atm)						
A	15.135	30.86	0.583917	4.526	1.026167	0.449867	0.312733	0.772417	0.479767	0.1915	0.064258	0.01621	0.003848
B	23.765	28.43333	0.5118	6.760833	1.59	0.787867	0.4511	1.116	0.809317	0.292933	0.083428	0.018167	0.003489
C	28.24333	19.87167	0.102855	3.297833	1.421833	0.683583	0.229883	0.288433	0.153367	0.072487	0.03679	0.015695	0.006824
D	18.00167	20.33167	0.20555	2.876333	1.002217	0.920633	0.166433	0.346817	0.19515	0.096233	0.048467	0.018225	0.009619
E	19.59	20.87833	0.062895	1.331333	0.9886	0.801567	0.175783	0.17145	0.096018	0.05361	0.037528	0.024118	0.009525
F	27.34333	18.315	0.187733	4.431	1.533667	1.168	0.2432	0.498717	0.379533	0.192333	0.085112	0.03181	0.012962
G	18.20333	31.59167	0.153133	1.991	0.951517	0.4767	0.41975	0.364117	0.157033	0.06153	0.030473	0.014423	0.007578
H	27.35167	29.895	0.15915	3.2845	1.458	0.879583	0.574783	0.5351	0.27985	0.118267	0.056978	0.024222	0.010832
CP*	22.34833	24.93667	0.203783	3.433333	1.253	0.700433	0.38475	0.592133	0.359483	0.13675	0.049615	0.01638	0.006019
R-H	27.22833	29.87833	0.164167	3.375167	1.491333	0.878583	0.530467	0.58495	0.332033	0.109967	0.037745	0.012445	0.004314
R-CP*	22.5	24.98333	0.192267	3.255	1.272167	0.738633	0.423133	0.570267	0.312567	0.116483	0.04154	0.01439	0.003798

* CP denotes center-point values

Table 5. Average of Inlet and Outlet Partial Pressures

Experiment Label	CO	H_2	H_2O	CO_2	N_2	HC	MeOH	EtOH	PrOH	BuOH	PenOH	HexOH	HeptOH
							(atm)						
A	18.0175	31.755	0.292	2.263	0.9486	0.2249	0.1564	0.3862	0.2399	0.0958	0.0321	8.11E-03	1.92E-03
B	27.3925	30.3717	0.2559	3.3804	1.4415	0.3939	0.2256	0.558	0.4047	0.1465	0.0417	9.08E-03	1.74E-03
C	29.7967	20.8208	0.0514	1.6489	1.3644	0.3418	0.1149	0.1442	0.0767	0.0362	0.0184	7.85E-03	3.41E-03
D	19.6108	21.2208	0.1028	1.4382	0.9434	0.4603	0.0832	0.1734	0.0976	0.0481	0.0242	9.11E-03	4.81E-03
E	20.395	21.4942	0.0314	0.6657	0.9472	0.4008	0.0879	0.0857	0.048	0.0268	0.0188	0.0121	4.76E-03
F	29.3467	20.0425	0.0939	2.2155	1.4203	0.584	0.1216	0.2494	0.1898	0.0962	0.0426	0.0159	6.48E-03
G	19.5517	32.1208	0.0766	0.9955	0.9113	0.2384	0.2099	0.1821	0.0785	0.0308	0.0152	7.21E-03	3.79E-03
H	29.1858	31.1025	0.0796	1.6423	1.3755	0.4398	0.2874	0.2676	0.1399	0.0591	0.0285	0.0121	5.42E-03
CP*	24.2342	26.0733	0.1019	1.7167	1.171	0.3502	0.1924	0.2961	0.1797	0.0684	0.0248	8.19E-03	3.01E-03
R-H	29.1092	31.0942	0.0821	1.6876	1.4077	0.4393	0.2652	0.2925	0.166	0.055	0.0189	6.22E-03	2.16E-03
R-CP*	24.3	26.0967	0.0961	1.6275	1.1936	0.3693	0.2116	0.2851	0.1563	0.0582	0.0208	7.20E-03	1.90E-03

* CP denotes center-point values