

KINETICS OF HIGHER-ALCOHOL FORMATION FROM SYNTHESIS GAS USING STATISTICALLY DESIGNED EXPERIMENTS

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Introduction

Alcohols containing upto five carbon atoms can be added to the gasoline pool to improve the octane number without an excessive impact on the environment. The Dow patents [1,2] describe a promoted molybdenum sulfide catalyst for the production of these alcohols from synthesis gas even in the presence of sulfur. Screening studies in our laboratory [3] have indicated that a carbon-supported, potassium-promoted cobalt-molybdenum sulfide catalyst yields exceptionally good results, in terms of the space-time yield (STY) of each higher alcohol.

For the purpose of reactor design, it is necessary to obtain a set of kinetic equations for this catalyst, to represent the formation rates of the alcohols in a range of realistic conditions for a large number of variables. However, the kinetic equations need not necessarily reflect the mechanism(s) of the reactions. The present work describes such a set of equations for methanol, ethanol, propanol and total hydrocarbons. The range of conditions used to obtain the experimental data, and in which the set of equations is valid, was based on the screening study and is characterized by: temperature, 300-350°C; total pressure, 400-1000psi; CO/H₂ ratio, 0.5-2; and methanol, 0-1.2ml/h. A fractional factorial set of experiments was designed to incorporate this large set of parameters. A Bertly-type internal-recycle reactor was used, to ensure that the reaction rate corresponded to known (outlet) concentrations of reactants and products.

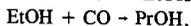
Experimental

The K-Co-MoS/C catalyst was prepared by incipient-wetness impregnation. The catalyst contained 18wt% Mo with a Co/Mo ratio of 0.34 and a K/Mo ratio of 1.3. The catalyst was reduced to the sulfide form inside the reactor, and thereafter purged in hydrogen. The reactor system is computer controlled and all operating conditions can be set by a PC. The system has four lines for gas feed and one line for the liquid methanol feed. The 16 factorial experiments were performed in random order, so as to make the catalyst age an independent variable as well. An additional, center-point, experiment was repeated after every four runs. Product STYs were obtained every 2h, and each experiment was conducted for at least 12h.

Results

The products were found to be linear alcohols, and follow an Anderson-Schultz-Flory distribution. A detailed examination of the experiments with methanol addition showed (1) that the higher alcohols are generated from secondary reactions involving methanol, (2) that a simple condensation reaction involving only alcohols can be ruled out, and (3) that the most likely process involves CO insertion into a lower-carbon-number alcohol to form a higher alcohol. These observations are consistent with the isotopic-labelling results of Santiesteban [4].

Based on this reaction scheme, a two-step process was used to obtain the kinetic equations. First, simple power-law representations were used to quantify the "gross" rates of formation of each of the alcohols (other than methanol) and the hydrocarbons. By the "gross" rate of formation, we refer to the total rate of formation, regardless of the fact that some of the particular species may react further. Then the rate of formation as actually measured (*i.e.*, after some of the particular species reacts further) would be the "net" rate of formation. Since we assume sequential reactions:



etc., therefore the "gross" rate of methanol formation is the sum of the "net" rates of methanol, ethanol, *etc.* formation, and so on.) For an alcohol of carbon number *n*, the power-law rate expression included terms for the partial pressures of CO, H₂, inert, and the alcohol of carbon number *n-1*, as well as terms for the catalyst age (*t*), the temperature (*T*), the pre-exponential

factor (A) and the activation energy (E). The general power-law expression used can be centered around the center-point values of the parameters as:

$$r_n^{\text{gross}} = k_n (P/P_{cp})_{\text{CO}}^{a_n} (P/P_{cp})_{\text{H}_2}^{b_n} (P/P_{cp})_I^{c_n} (P/P_{cp})_{n-1}^{d_n} (t/t_{cp})^{-\lambda_n} \quad (1a)$$

where

$$k_n = A_n \exp[-(E_n/R)(1/T - 1/T_{cp})] \quad (1b)$$

Here the subscripts I and cp denote inert and a center-point value respectively. Note that a power-law expression for methanol, for which $n=1$, was not obtained in this first step. Because methanol is used as a reactant in many of the runs in this work, the rate of formation could be positive or negative, and a simple power-law model cannot be used for this purpose. For the other alcohols, the best fit of the power-law models yield values of A_n , E_n , a_n - d_n , and λ_n as shown in Table I. Further, a statistical analysis of the results indicated which parameters were statistically significant for each product. These parameters are identified in Table I.

These parameters were then used in the second step, where a Langmuir-Hinshelwood-type rate expression was used for each product, incorporating only the statistically significant parameters for each product. Now a methanol rate expression can be written, incorporating both forward- and reverse-reaction terms to allow for net rates of formation or net rates of reaction. Kinetic rate constants, equilibrium constants, and activation energy constants representing each statistically significant parameter were obtained by a non-linear best fit of the Langmuir-Hinshelwood-type rate expression. The final expressions can be written as:

$$r_{\text{MeOH}}^{\text{gross}} = \frac{4.9047 \exp[-(117 \times 10^3/R)(1/T - 1/T_{cp})] \{ \pi_{\text{CO}} \pi_{\text{H}_2}^2 - (0.3359 K_{cp}/K_{eq}) \pi_{\text{MeOH}} \}}{(1 + 0.0696 \pi_{\text{CO}} + 0.64 \pi_{\text{H}_2}^2 + 0.694 \pi_{\text{MeOH}})^2} \quad (2)$$

$$r_{\text{EtOH}}^{\text{gross}} = \frac{1.5259 \exp[-(25.0 \times 10^3/R)(1/T - 1/T_{cp})] \pi_{\text{MeOH}}}{1 + 0.7367 \pi_{\text{MeOH}}} \quad (3)$$

$$r_{\text{PrOH}}^{\text{gross}} = \frac{0.1159 \exp[-(86.8 \times 10^3/R)(1/T - 1/T_{cp})] \pi_{\text{EtOH}}}{1 + 0.640 \pi_{\text{EtOH}}} \quad (4)$$

$$r_{\text{HC}}^{\text{gross}} = \frac{4.6965 \exp[-(95.3 \times 10^3/R)(1/T - 1/T_{cp})] \pi_{\text{MeOH}}}{1 + 1.2479 \pi_{\text{MeOH}}} \quad (5)$$

Conclusions

The forms of the final rate expressions obtained imply that, under the present conditions, the rate expressions refer to the intrinsic kinetics and are not strongly governed by internal pore diffusion. Further, it would appear that the chemisorption of alcohol is the rate-limiting step, and that the individual steps of hydrogen cleavage, hydrogenation, dehydration and CO insertion (in the overall CO-insertion mechanism) are not rate limiting.

Acknowledgments

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References

1. M.M. Conway, C.B. Murchison and R.R. Stevens, *US Patent 4,675,344*, (1987).
2. R.R. Stevens, *US Patent 4,752,622* (1988).
3. Z. Liu, X. Li, M.R. Close, E.L. Kugler, J.L. Petersen and D.B. Dadyburjor, *Ind. Eng. Chem. Res.*, submitted (1996).
4. J.G. Santiesteban, Ph.D. Dissertation, Lehigh University (1989).

Table I
 Results of Fit to Power-Law Model for Gross Reaction Rates

Species	A_n	E_n	a_n	b_n	c_n	d_n	h_n
Ethanol	0.959	-38,252	0.1242	-0.3067	-0.0411	0.7307(*)	-0.1511
Propanol	0.0904	-97,852	0.0893	-0.6406	0.0216	0.5642(*)	-0.3226
Hydrocarbons	2.68	-106,478	-0.0273	-0.5212(*)	-0.0123	0.6636(*)	-0.2682(*)

(*) These parameters considered statistically significant