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Microkinetic Study of Syngas Conversion to Dimethyl Ether over a Bifunctional Catalyst: CZA/FER

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Abstract Dimethyl ether (DME) is an environmentally friendly fuel and economical compound that can be synthesized through methanol (MeOH) dehydration or direct synthesis from syngas via the water-gas shift reaction. Catalysts such as CZA for syngas conversion to MeOH and zeolites or $\gamma - Al_2O_3$ for MeOH dehydration are necessary for these reactions. A hybrid catalyst,

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CZA/FER, can be used to directly convert syngas into DME via MeOH. While previous studies have developed kinetic models for these catalytic reaction systems using lumped or microkinetic models, differences in describing elementary reactions have led to variations in detail. In this study, we developed a microkinetic model for DME synthesis from syngas via MeOH over a CZA/FER hybrid bifunctional catalyst. We considered detailed reaction rates and site fractions to determine the dominance of DME synthesis path between the associative and dissociative paths. The model is based on a two-site fraction model for each catalyst, with 28 reactions over CZA and nine reactions over FER. Reaction parameters were determined using transition state theory (TST) and the UBI-QEP method for CZA and the second-order Møller-Plesset perturbation theory (MP2) for FER The pre-exponential factors of Arrhenius rate constants were estimated with experimental data at 250 ℃, which supported the model's accuracy. Our results showed that the associative pathway is dominant for DME synthesis over a CZA/FER hybrid catalyst, which differs from our previous research on microkinetic modeling for MeOH dehydration to DME over a FER zeolite. We also suggest an operating condition range for converting CO_2 in the feed. We compare the relative reaction rates of elementary reactions and site fractions in each catalyst to enhance the understanding of the catalytic reaction system.

Keywords C1 Chemistry · Dimethyl ether · Kinetic modeling · Microkinetics · Hybrid bifunctional catlayst

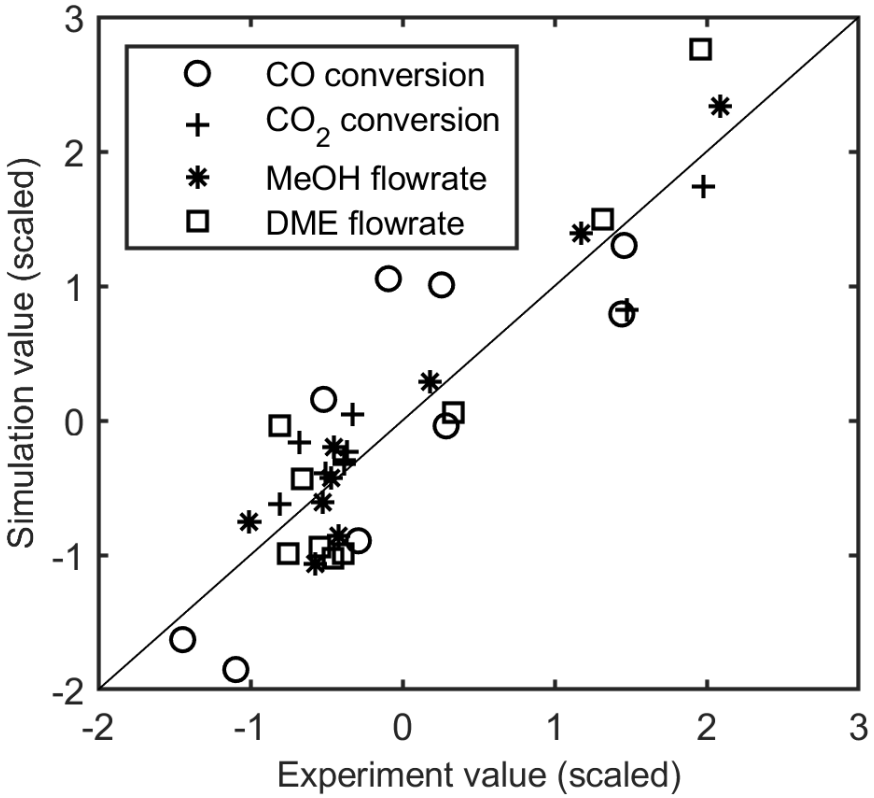

Fig. 1: Parity plot made by scaled with nomalizing elements in objective function of developed microkinetic model.

Fig. 1 shows a parity plot of the microkinetic model developed in this study. The plot consists of 36 points, with nine points for each of the following parameters: CO conversion, CO_2 conversion, MeOH flowrate, and DME flowrate. Each element of the plot is normalized using the mean and standard deviation of the experimental data. Table 1 contains the raw and normalized data for the CO conversion, CO_2 conversion, MeOH flowrate, and DME flowrate obtained from both experiments and the model.

Table 1: The raw data and normalized data of CO conversion, CO_2 conversion, MeOH flowrate and DME flowrate of experiments and calulated by model.

		Exp1	Exp2	Exp3	Exp4	Exp5	Exp6	Exp7	Exp8	Exp9	Mean	Std. Dev.
CO conversion [%]	Exp	88.60	69.50	80.90	88.50	75.60	77.10	71.80	78.40	80.70	79.01	6.58
	Model	87.58	68.29	78.75	84.22	80.04	73.13	66.83	85.95	85.65	-	-
CO_2 conversion [%]	Exp	-18.00	-29.00	-22.10	-26.00	-18.80	-19.20	-19.30	23.30	34.80	-10.48	22.89
	Model	-9.37	-24.68	-19.38	-14.27	-15.82	-17.21	-17.88	8.38	29.32	-	-
MeOH flowrate [10^{-8} mol/s]	Exp	6.187	11.92	11.75	11.16	18.38	28.49	37.86	12.25	10.64	16.52	10.21
	Model	8.791	14.48	12.13	10.28	19.48	30.74	40.35	7.783	5.644	-	-
DME flowrate [mol/s]	Exp	8.267	5.622	7.144	7.772	13.57	20.79	25.54	6.261	5.183	11.13	7.345
	Model	3.873	3.873	4.225	3.594	11.55	22.13	31.39	7.927	10.86	-	-
CO conversion [Normalized]	Exp	1.457	-1.445	0.287	1.442	-0.518	-0.290	-1.096	-0.093	0.257	-	-
	Model	1.302	-1.629	-0.040	0.792	0.157	-0.894	-1.852	1.054	1.008	-	-
CO_2 conversion [Normalized]	Exp	-0.329	-0.809	-0.508	-0.678	-0.364	-0.381	-0.385	1.476	1.978	-	-
	Model	0.049	-0.620	-0.389	-0.166	-0.233	-0.294	-0.323	0.824	1.739	-	-
MeOH flowrate [Normalized]	Exp	-1.011	-0.450	-0.466	-0.524	0.183	1.173	2.090	-0.418	-0.575	-	-
	Model	-0.756	-0.200	-0.429	-0.611	0.290	1.393	2.334	-0.855	-1.065	-	-
DME flowrate [Normalized]	Exp	-0.389	-0.749	-0.542	-0.457	0.332	1.315	1.962	-0.662	-0.809	-	-
	Model	-0.988	-0.988	-0.940	-1.026	0.057	1.498	2.758	-0.436	-0.036	-	-

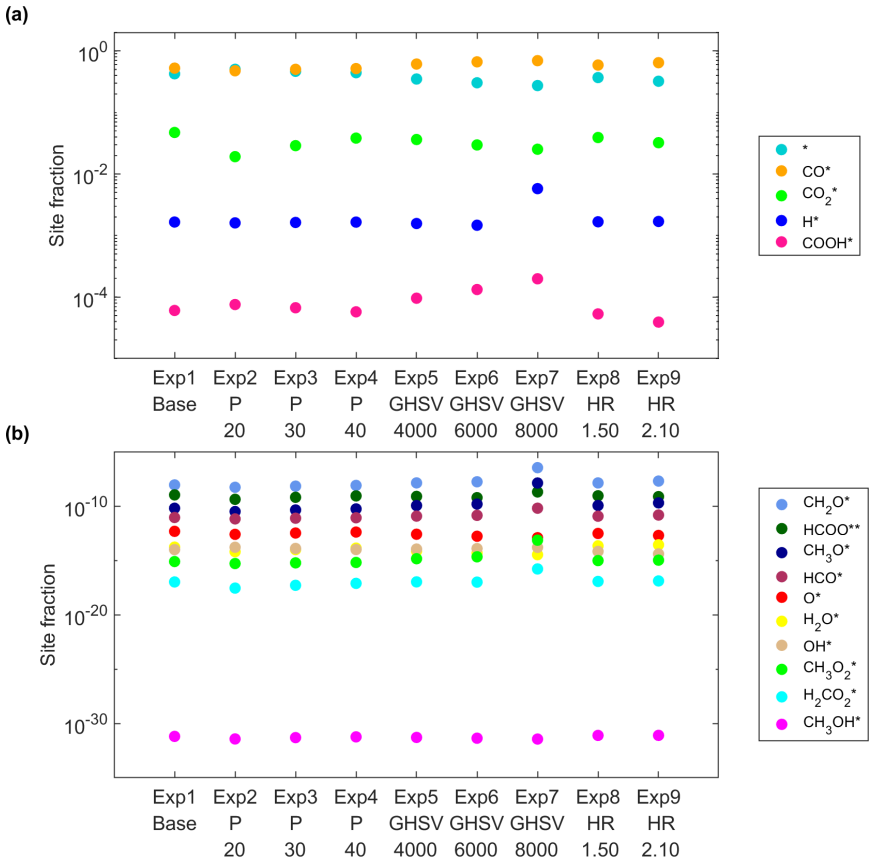

Fig. 2: Site fraction based on the result of the simulation using microkinetic model: site fraction on CZA. HR means the hydrogen ratio = $H_2/(2CO + 3CO_2)$ in feed. (a) major components: site fractions that are greater than 10^{-8} (b) minor components: site fractions that are less than 10^{-8}

Fig. 2 and 3 present the site fractions obtained from the microkinetic model simulation, with the corresponding raw data included in Tables 2 and 3, respectively.

The site fractions over CZA are depicted in Fig. 2, where the major and minor components were determined based on the criterion of 10^{-8}. The major components, which are greater than 10^{-8}, are displayed in (a), while the minor components, which are less than 10^{-8}, are shown in (b).

In Fig. 3, the site fractions over FER are shown. The major and minor components were determined using the criterion of 10^{-10}. The major components, which are greater than 10^{-10}, are displayed in (a), while the minor components, which are less than 10^{-10}, are shown in (b).

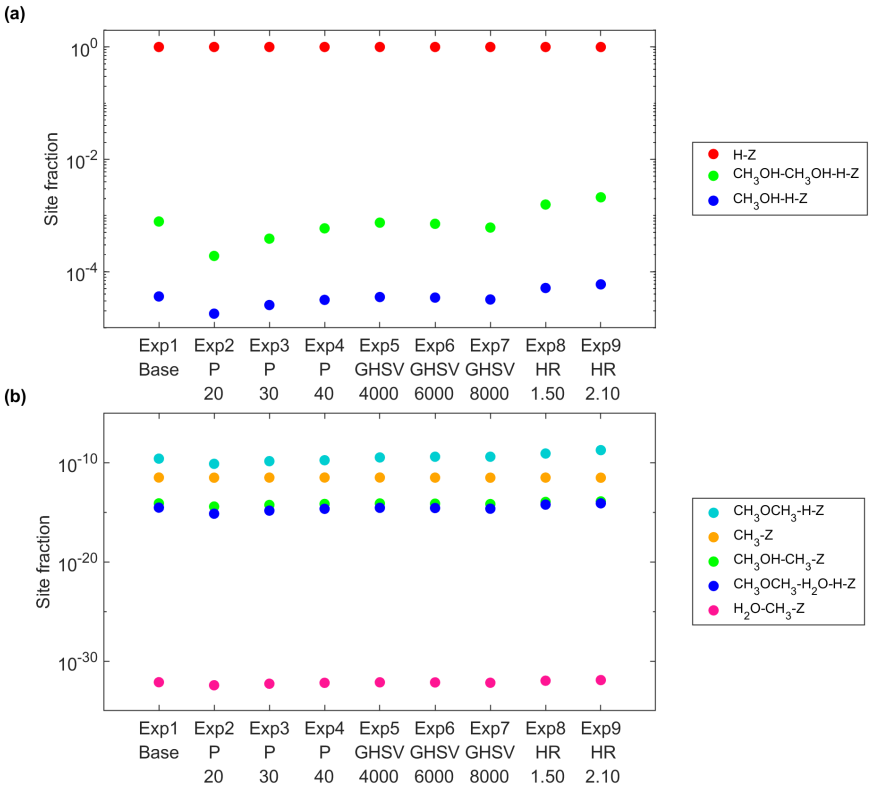

Fig. 3: Site fraction based on the result of the simulation using microkinetic model: site fraction on FER. HR means the hydrogen ratio = $H_2/(2CO + 3CO_2)$ in feed. (a) major components: site fractions that are greater than 10^{-10} (b) minor components: site fractions that are less than 10^{-10}

Table 2: Site fraction based on the result of the simulation using microkinetic model: site fractions on CZA.

component	Exp1	Exp2	Exp3	Exp4	Exp5	Exp6	Exp7	Exp8	Exp9
* (vacant)	4.254E-01	5.032E-01	4.666E-01	4.431E-01	3.498E-01	3.039E-01	2.737E-01	3.693E-01	3.218E-01
CO*	5.256E-01	4.760E-01	5.029E-01	5.170E-01	6.122E-01	6.649E-01	6.951E-01	5.899E-01	6.442E-01
CO_2*	4.729E-02	1.913E-02	2.887E-02	3.827E-02	3.631E-02	2.964E-02	2.524E-02	3.914E-02	3.224E-02
H*	1.655E-03	1.603E-03	1.629E-03	1.650E-03	1.565E-03	1.468E-03	5.778E-03	1.669E-03	1.690E-03
COOH*	6.039E-05	7.544E-05	6.686E-05	5.742E-05	9.558E-05	1.323E-04	1.978E-04	5.308E-05	3.911E-05
CH_2O*	8.747E-09	5.312E-09	6.741E-09	7.889E-09	1.344E-08	1.703E-08	3.384E-07	1.336E-08	1.983E-08
HCOO**	1.057E-09	4.141E-10	6.353E-10	8.531E-10	7.676E-10	5.876E-10	1.970E-09	8.824E-10	7.358E-10
CH_3O	6.283E-11	3.123E-11	4.345E-11	5.426E-11	1.109E-10	1.518E-10	1.311E-08	1.125E-10	1.952E-10
HCO*	8.823E-12	6.544E-12	7.577E-12	8.311E-12	1.179E-11	1.384E-11	6.294E-11	1.160E-11	1.481E-11
O*	4.692E-13	2.479E-13	3.284E-13	4.021E-13	2.543E-13	1.660E-13	1.215E-13	3.003E-13	1.973E-13
H_2O*	1.657E-14	6.268E-15	9.756E-15	1.345E-14	7.108E-15	4.747E-15	3.345E-15	2.174E-14	2.711E-14
OH*	9.856E-15	1.608E-14	1.251E-14	9.924E-15	1.101E-14	1.219E-14	1.571E-14	6.700E-15	3.939E-15
CH_3O_2*	7.807E-16	5.117E-16	5.921E-16	6.435E-16	1.418E-15	2.130E-15	7.239E-14	9.578E-16	1.046E-15
H_2CO_2*	1.035E-17	2.808E-18	5.091E-18	7.681E-18	1.051E-17	1.000E-17	1.628E-16	1.157E-17	1.286E-17
CH_3OH*	6.400E-32	3.739E-32	4.939E-32	5.794E-32	5.141E-32	4.361E-32	3.636E-32	7.870E-32	7.960E-32

Table 3: Site fraction based on the result of the simulation using microkinetic model: site fractions on FER.

component	Exp1	Exp2	Exp3	Exp4	Exp5	Exp6	Exp7	Exp8	Exp9
H-Z	9.992E-01	9.998E-01	9.996E-01	9.994E-01	9.992E-01	9.993E-01	9.994E-01	9.984E-01	9.978E-01
CH_3OH-CH_3OH-H-Z	7.812E-04	1.906E-04	3.870E-04	5.905E-04	7.454E-04	7.112E-04	6.096E-04	1.567E-03	2.109E-03
CH_3OH-H-Z	3.619E-05	1.788E-05	2.548E-05	3.147E-05	3.536E-05	3.453E-05	3.197E-05	5.124E-05	5.943E-05
CH_3OCH_3-H-Z	2.487E-10	7.462E-11	1.384E-10	1.717E-10	3.270E-10	3.879E-10	3.879E-10	8.140E-10	1.784E-09
CH_3-Z	3.115E-12	3.002E-12	3.065E-12	3.112E-12	3.112E-12	3.040E-12	3.001E-12	3.067E-12	2.986E-12
CH_3OH-CH_3-Z	7.787E-15	3.706E-15	5.392E-15	6.762E-15	7.599E-15	7.250E-15	6.626E-15	1.086E-14	1.227E-14
CH_3OCH_3-H_2O-H-Z	2.897E-15	7.067E-16	1.435E-15	2.189E-15	2.764E-15	2.637E-15	2.260E-15	5.809E-15	7.820E-15
H_2O-CH_3-Z	7.453E-33	3.683E-33	5.247E-33	6.480E-33	7.281E-33	7.111E-33	6.584E-33	1.055E-32	1.224E-32