Modeling of Iron Catalyst Deactivation and the Impact of Different Promoters on this Model

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Abstract: The synthesis of Fischer Tropsch is a catalytic process converting synthesis gas to liquid fuels. Iron catalytic activity changed due to the increase in metals as a promoter. The catalyst was determined at a temperature of 280 ° and the ratio of H2/CO = 2/1, and the metals were added to the catalyst including Mn, Cr, Mo, Ta, V and Zr. The rate of the catalyst deactivation was investigated and specified. The catalyst deactivation model followed the first order GPLE model and the catalyst FeZr is deactivated earlier than other catalysts.
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1. Introduction

The synthesis of Fischer-Tropsch is a catalytic process converting the synthesis gas, which is obtained from coal or natural gas, to portable fuels and petrochemical reserve [1-6]. Iron catalysts are more suitable to produce long-chain hydrocarbons than cobalt catalysts. Iron catalysts reaction conditions occur at low temperature and their prices are cheaper [6,7]. For Iron catalysts, the increase in water to the feed in the partial pressure FTS reaction has affected CO and hydrogen in the reactor [7,8]. The catalysts activities, selectivity and the catalyst life are all influenced by factors such as the nature and the basic structure, adsorption or loading metal and preparation of catalyst [9]. Most studies have been indicated the improvement of iron catalysts activities, which is obtained from transition metals [10]. Pendyala showed the effect of water on iron catalysts [8]. Eliason studied the reaction and kinetics of inactivation of Fischer-Tropsch synthesis on iron catalysts without and with a potassium promoter [11]. The article investigates the rate of catalyst deactivation due to the increase in such promoters as Mn, Ta, Cr, Zr and V.

2. Experimental

The general formula of the base catalyst of the synthesis is based on Fe100/5Cu/17Si. Me represents the third transition metal in the Fe95/5Me/5Cu/17Si formula. Fe100/5Cu/17Si, Fe (NO3)3•9H2O and CuN2O6•3H2O are first dissolved in 60 ml of water while tetraethylorthosilicate (Si (OC2H5), TEOS) is dissolved in 40 ml of Propanol. The solution is mixed and 100 ml of the final solution is achieved. Thus, the final solution is heated. More detailed description was stated in [10].

3. Results and discussion

3.1. the rate of deactivation of the data

The catalyst activity was determined at a temperature of 280 ° and the ratio of H2 / CO = 2/1 [10]. Table 1 showed the deactivation of the catalyst Fe 100. TOS (Time On Stream).

Table 1. The data related to deactivation rate of Fe 100 catalyst

TOS	Activity
0	1
14.5089	0.930236
42.6197	0.869567
69.8234	0.826405
98.8414	0.756993
126.9524	0.713854
155.9694	0.661972
184.9874	0.653913
213.0984	0.619539
241.2094	0.611458
269.3204	0.559555
326.4484	0.543415

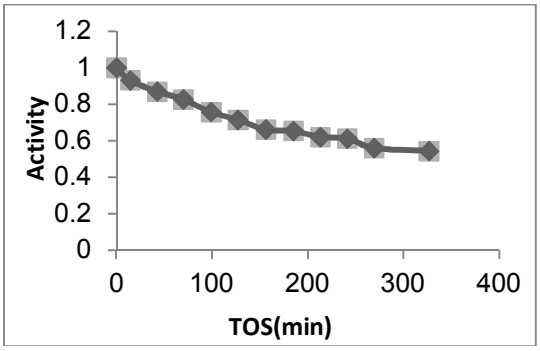

Fig 1. Deactivation rate of Fe 100 catalyst

Table 2 indicated the data of deactivation of the catalyst FeCr and Figure 2 represented the rate of the catalyst deactivation [10]. In this Figure, the catalyst activity was stabled at 0.28.

Table 2. The data related to deactivation rate of FeCr catalyst

TOS	Activity
0	1
14.368	0.824789
42.3689	0.688038
69.4664	0.555557
99.3394	0.491454
127.4124	0.444446
155.4754	0.384616
185.3964	0.380343
212.5864	0.363249
240.6804	0.341882
298.6984	0.320514
326.7814	0.286325

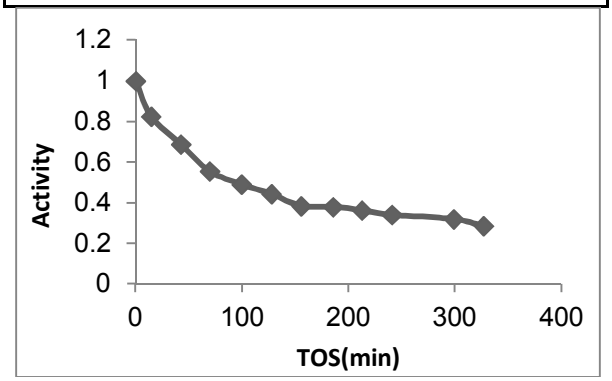

Fig 2. deactivation rate of FeCr catalyst

Table 3 showed the data of deactivation of the catalyst FeMn and Figure 3 represented the rate of the catalyst deactivation [10]. Mn has the industrial benefit amongst the iron promoters and has been extensively studied in recent years [12-14]. The increase in the average amount of manganese enhanced the iron's catalytic activity [15].

Table 3. The data related to deactivation rate of FeMn catalyst

TOS	Activity
0	1
13.6021	0.854919
43.5265	0.735663
71.6372	0.654833
99.7482	0.591087
128.7662	0.552985
156.8762	0.523416
185.8942	0.506672
213.0982	0.494179
242.1162	0.48598
297.4312	0.465277
271.1332	0.460693

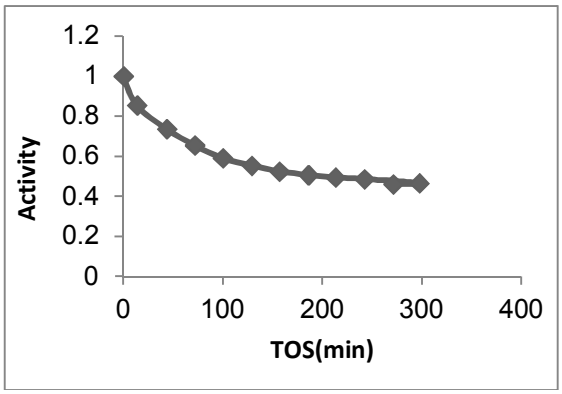

Fig 3. Deactivation rate of FeMn catalyst

Table 4 indicated the data of deactivation of the catalyst FeMo and Figure 4 showed the rate of the catalyst deactivation [10]. After 30 minutes, the catalyst was stabled at 0.4. The increase in Mo prevented agglomeration of iron particles [16]. The dispersion of promoter Mo prevented agglomeration of the active sites [17]. The metal Mo had a good hydrogenation activity and decreased the rate of deactivation by preventing the formation of coke [16, 17].

Table 4. The data related to deactivation rate of FeMo catalyst

TOS	Activity
0	1
13.6021	0.83721
41.7129	0.767442
70.7304	0.651163
99.7484	0.589148
127.8594	0.542636
155.9694	0.503876
184.0804	0.488372
214.0054	0.472868
241.2094	0.457365
269.3204	0.434109
298.3374	0.410853

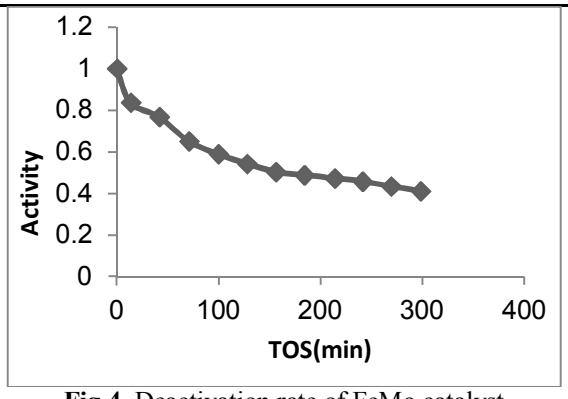

Fig 4. Deactivation rate of FeMo catalyst

Table 5 showed the data of deactivation of the catalyst FeTa and Figure 5 represented the rate of the catalyst deactivation [10].

Table 5. The data related to deactivation rate of FeTa catalyst

TOS	Activity
0	1
13.6021	0.878051
42.6197	0.777978
70.7304	0.65632
99.7484	0.599384
127.8594	0.53524
155.9694	0.463908
184.0804	0.45728
213.0984	0.44348
241.2094	0.422473
270.2264	0.415864
297.4304	0.394838

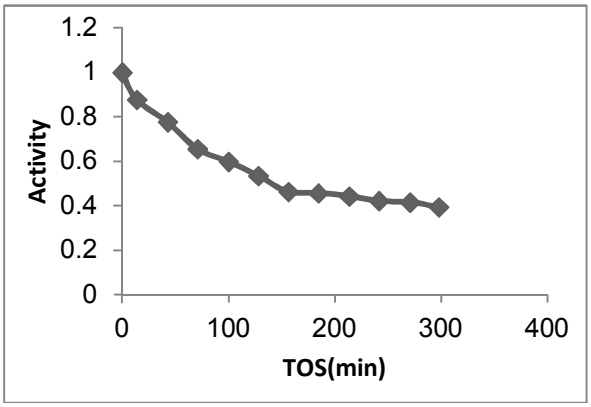

Fig 5. Deactivation rate of FeTa catalyst

Table 6 indicated the data of deactivation of the catalyst FeV and Figure 6 showed the rate of the catalyst deactivation [10].

Table 6. The data related to deactivation rate of FeV catalyst

TOS	Activity
0	1
14.5637	0.899999
42.7398	0.78125
70.9059	0.68125
99.9649	0.60625
128.1029	0.556249
156.2509	0.487499
213.3939	0.462499
241.5079	0.456249
269.6359	0.424999
326.7849	0.387499

Table 7 showed the data of deactivation of the catalyst FeZr and Figure 7 showed the rate of the catalyst deactivation [10]. The promoter had a great impact on catalytic activity [18].

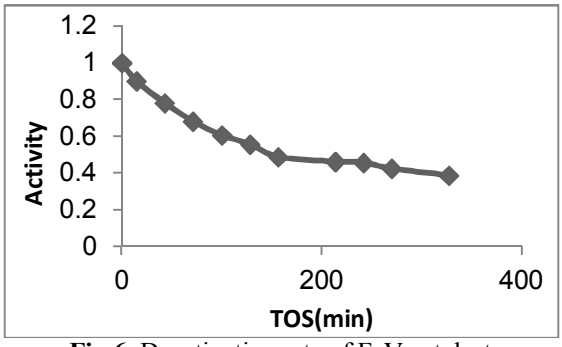

Fig 6. Deactivation rate of FeV catalyst

Table 7. The data related to deactivation rate of FeZr catalyst

TOS	Activity
0	1
13.6021	0.769232
41.7129	0.630767
70.7304	0.53846
98.8414	0.473076
126.9524	0.423076
155.9694	0.380769
184.0804	0.353846
212.1914	0.365384
241.2094	0.342307
270.2264	0.338461
297.4304	0.31923

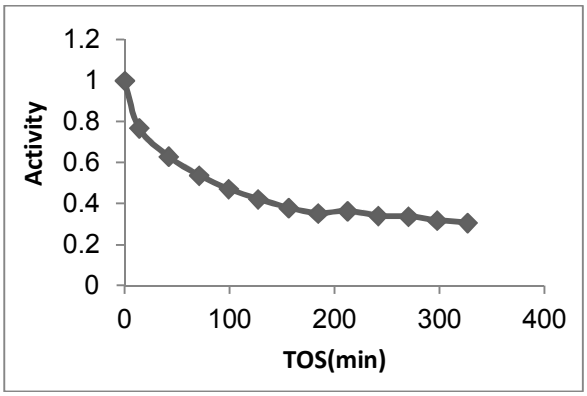

Fig 7. Deactivation rate of FeZr catalyst

3.2. the deactivation model

The catalysts followed the first order GPLE model (General Power Law Expression) in which kd is the constant factor of deactivation and ain is the steady state activity over long time on stream (TOS) [19, 20].

a (t)= (1-ain) exp (-kdt) +ain (1)

The more the kd, the more the deactivation rate. Although Lohitharn perceived that the increase transition metals enhanced the catalytic activity and the catalytic activity was described as FeMn>FeZr>FeCr>FeV>FeTa>FeMo>Fe100 [10] while deactivation rate was propounded as FeZr>FeMn>FeCr>FeMo>FeTa>FeV>Fe100, that is, the catalyst FeZr was deactivated earlier than the rest of the catalysts.

Table 8. Deactivation parameters for model GPLE

Catalyst	Order GPLE	k_d	a_{in}	R^2
Fe100	1	0.006	0.4809284	0.9931136
FeCr	1	0.014	0.3153819	0.9912709
FeMn	1	0.015	0.4647163	0.9910004
FeMo	1	0.013	0.420861	0.9843102
FeTa	1	0.011	0.378582	0.9945776
FeV	1	0.0103	0.3849579	0.9963612
FeZr	1	0.018	0.3351547	0.9793809

4. Conclusion

The increase in transition metals to the catalyst Fe100 enhanced the catalytic activity. The catalyst is prepared at a temperature of 280 ° and the ratio of H_2/CO=2/1. The deactivation rate was determined for the catalyst. The importance of the deactivation models were described in predicting the rate of the reactions with time, the detailed design of reactors and industrial applications of the models. After we have the models, it was found that the catalysts followed the first order GPLE model and after comparing them, it was determined that the highest rate of deactivation belonged to catalyst FeZr and the lowest rate of deactivation belonged to the catalyst Fe100. While promoters enhance the catalytic activity, it can increase the rate of deactivation in some cases.

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