Supporting information

1 Mathematical solution for 1D model and its application in deactivation of ZSM-12

When considering the basic model of 1D network, we can get the analytical solution from the principle of probability theory.

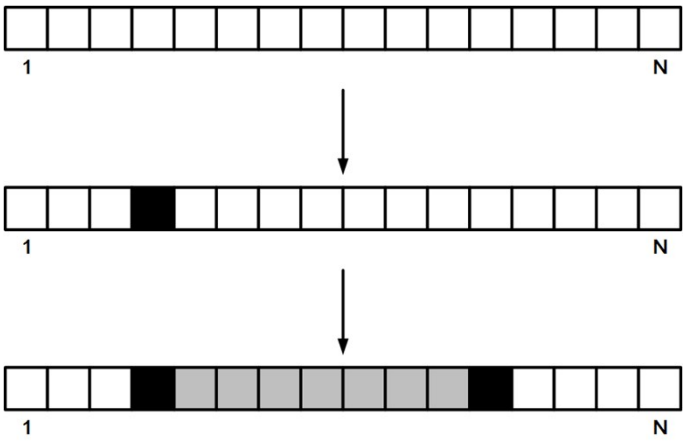

Figure S1 brief concept of 1D model.

Figure S1 gives the brief concept of 1D model. We assume that the number of cages is N, and each cage has a deactivation probability of p. Time is described as number of steps m. the detailed process is at each step, a random number is generated to determine whether the cage is deactivated or not. After this step, the most left cage and most right cage which is deactivated are determined, and all the cages between them are labeled as deactivated.

With the traditional probability theory, we can calculate the probability of n cages alive at step m: $P(n,m)$. If $(N-n) \geq 2$, means there are at least 2 cage deactivated, there exists a continuous deactivation chain. $(n+1)$ kinds of different position can be considered. Alive cages should not deactivate, so there is a factor of $(1-p)^{mn}$. the two boundary cages should deactivate at any step before this, so there is a factor of $\left(1-(1-p)^{m}\right)^{2}$. The inner cages can be any state, because they are blocked. We assume $Q=(1-p)^{m}$, we get $P(n,m)=Q^{n}(1-Q)^{2}(n+1), n \leq N-2$. When $n=N-1$, similarly we can get $P(N-1,m)=N(1-Q)Q^{N-1}$. And $P(N,m)=Q^{N}$.

$$P(n)=\begin{cases} Q^n(1-Q)^2(n+1) & n\le N-2 \\ N(1-Q)Q^{N-1} & n=N-1 \\ Q^N & n=N \end{cases}$$

As for there are huge number of channels in zeolites in normal experimental conditions, the average alive length can be predicted by mathematical expectation. The average alive percentage follows:

$$C=\frac{E(m)}{N}$$

C follows:

$$C=\frac{(2Q^N-NQ^N-2)Q+NQ^N}{N(Q-1)}$$

We also assumed a first order kinetics as:

$$\frac{dX}{d\tau}=k(1-X)$$

X is the conversion and τ is the contact time. The contact time changes with time because of the deactivation process:

$$\tau=f(t)=C(bt)\tau_0$$

Integrate, we can get:

$$\ln\frac{1-X_0}{1-X}=k(\tau-\tau_0)$$

We can merge the constants and get:

$$X=1-Ae^{D\cdot C(bt)}$$

With the formula of C and some curve fitting, we can compare it with results of ZSM-12.

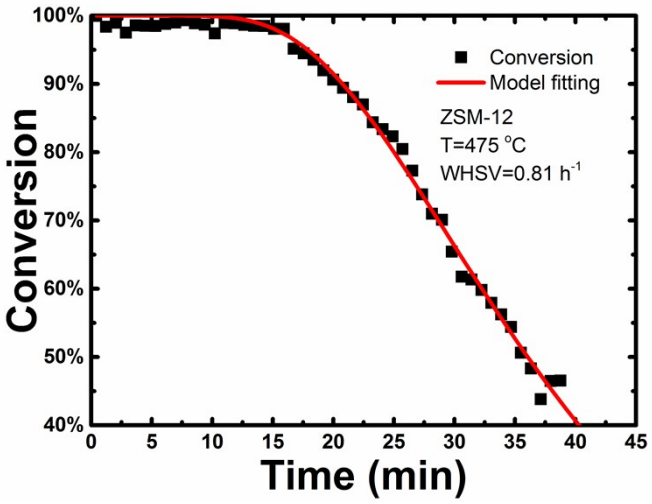

Figure S2 Comparison between model and experimental results. ZSM-12 was synthesized with Si/Al =40, and the crystal size of it was about 50 nm. Catalyst test of ZSM-12 was performed at 475 ℃,

with WHSV=0.81 h^{-1}. In the model, N was set to 100 considering the crystal size, and other parameters were empirical.

Figure S2 gives the comparison. We can conclude that the model is validated to 1D channel systems like ZSM-12.

2 Empirical calculation of 4-stage kinetics in deactivation model of SAPO-34

Our simple 4-stage first order kinetics can be described as the following matrix form

$$\frac{d}{dt}\begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} = \begin{bmatrix} k_1 C_{MeOH} \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} -k_2 & 0 & 0 \\ k_2 & -k_3 & 0 \\ 0 & k_3 & 0 \end{bmatrix} \cdot \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix}$$

We got the analytical solution for the above differential equation with Wolfram Mathmatica, and it is too long to put here. We collected coked SAPO-34 catalysts at different TOS, and detection of inner coke species was performed. Based on this, we get the empirical parameter with nonlinear curve fitting.

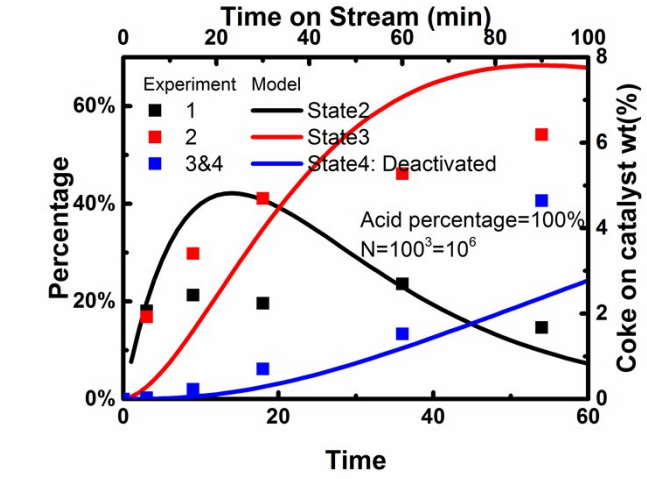

Figure S3 model results show agreements to the coke analysis.

Figure S3 gives the model results and the experimental results on carbon accumulation by time. There exists some deviation and this may because the carbon analysis was not quite and the model is too simple.