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Evaluation of H-ZSM-5 Deactivation During Dimethyl Ether to Hydrocarbons Transformation Process

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Hydrocarbons synthesis using transformation of methanol/dimethyl ether is of particular interest in connection with the possibility of using synthesized hydrocarbons not only as fuel but as components for basic organic synthesis to obtain organic acids, polymers and pharmaceuticals. However, catalysts deactivation, based on surface coking and dealumination, can be considered as one of the main problems for the wide application of this technology. Deactivation kinetics modeling can play a leading role for economic assessment of this process and for development of methods for catalysts activity and stability improving. Article devoted to approval three deactivation models. Simple linear deactivation model showed the possibility of its usage only in the first parts of the deactivation process, where kinetic curves are linear. An extra operator addition to this model for determination of deactivation rate change allowed to improve model reliability. To enhance model correlation with reaction mechanism additional model was developed using chemical equations for catalysts surface deactivation. This model application allowed to improve results accuracy, however measurement of surface active sites quantity is needed for this calculations

1. Introduction

Widespread depletion of traditional hydrocarbons sources (Smejkal, Q. et al., 2009) determines the need to develop and optimize methods (Ekhtiari, A. et al., 2019) for their synthesis from low-value or renewable sources of raw materials. The main techniques for producing synthetic hydrocarbons are the Fischer-Tropsch process (Wood, D.A. et al., 2012), which includes the production of hydrocarbons from syngas (Santos R.G. et al., 2020). The other method includes the production of hydrocarbons by transforming methanol or dimethyl ether obtained from syngas (Chotiwan, S. et al., 2019). Fischer-Tropsch reaction basically leads to the formation of linear hydrocarbons applicable as diesel fuel or raw material for further isomerization to form gasoline (Macheli, L. et al., 2021). Catalytic transformation of methanol (Jiang, J. at al., 2020) makes it possible to obtain a wider range of hydrocarbons (Chen, D., at al., 2012), including olefins, aliphatic and aromatic hydrocarbons (Pérez-Uriarte, P. at al., 2016). Obtaining liquid hydrocarbons by a transformation of methanol/dimethyl ether is of particular interest in connection with the possibility of using synthesized hydrocarbons not only as fuel but as components for basic organic synthesis to obtain organic acids, polymers, and pharmaceuticals (Kianfar, E. at al., 2020). However, catalysts deactivation because surface coking and dealumination can be considered as one of the main problems (Chen, D., at al., 2012), for wide application of this technology in industry (Khanmohammadi M. at al., 2016). Zeolite activity in methanol to hydrocarbons transformation process is typically attributed to Brønsted acidity (Zhao, S.F., at al., 2012). Therefore, decrees of catalyst acidity and quantity of Brønsted acid sites (Rojo-Gama, D. at al. 2017) can decrease process activity (Hwang, A. at al., 2019). The other possible options for deactivating the zeolite in the methanol to hydrocarbon transformation process may be the formation of silicon and aluminum carbides that are not active in the process of methanol transformation into hydrocarbons (Wan Z. at al., 2019). On the other hand, reversible deactivation of zeolites in methanol or dimethyl ether to hydrocarbons transformation process takes place in case of heavy polyaromatic compounds (Cordero-Lanzac, T. at al., 2018) adsorption

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on the surface of the active sites or in the zeolite channel (Pérez-Uriarte, P. at al., 2017), which in the first causes the loss of activity of only one active center (Janssens, T.V.W. at al., 2013), and in the second case, it can lead to the loss of several active sites activity (Chen, D., at al., 2012). Therefore, a study of zeolites, especially H-ZSM-5, deactivation kinetics particularities is of special interest for applying methanol to hydrocarbons transformation process in the industry and for development of the proper mechanism of this process.

2. Materials and methods

2.1 Materials

Methanol of chemical grade purity (99.9 wt. %) was purchased from Vectron (Russia), chemical grade purity alumina (99.1 wt.%) was purchased from Redkino catalyst factory (Russia), H-ZSM-5 (Si/Al=50, average crystal size is 30 μm) zeolite was purchased from HRC inc. (China). Ammonia chloride (99.5 wt.%) was purchased from Reachim (Russia). To transfer H-ZSM-5 zeolite in acidic form samples of zeolite were washed with 1M ammonia chloride in water then washed with distillate water dried at 70°C for a night than at 105°C, and a further sample was calcined 600°C, cooled to room temperature.

2.2 Methanol transformation reactor set up

Methanol at a flow rate of 0.1 ml/min by pump 7 is fed in mixer 6, heated to the required temperature (350 ° C), and filled with glass beads to form methanol vapor (Figure 1). Then methanol enters reactor 8, also heated to 350 ° C, filled with aluminum oxide, where dimethyl ether is synthesized, which is separated from water and methanol in refrigerator 9 and enters into reactor 10, heated to 350 °C, filled with zeolite. Gas samples are taken at a frequency of once an hour by an automatic dispenser of the chromatograph. Liquid samples are taken in accordance with the experimental procedure. The liquid hydrocarbons analysis was carried out using a Shimadzu HPMS2010 gas chromatography-mass spectrometer, and chromatograph Crystal 2000M. Zeolite regeneration was provided by purging reactor heated up to 600°C with air for 6 hours.

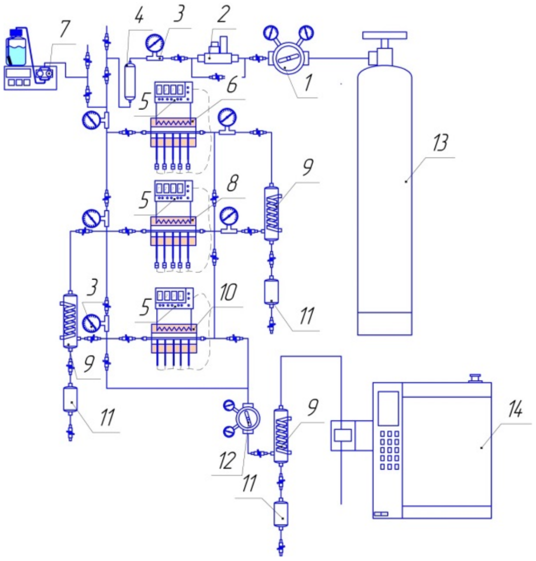


Figure 1. Reaction set up for methanol to hydrocarbons catalytic transformation:

1 - nitrogen pressure reducer, 2 - nitrogen mass flow meter, 3 - manometer, 4 - buffer tank, 5 - temperature controller, 6 - evaporator, 7 - pump for methanol supply, 8 - dimethyl ether synthesis reactor, 9 - refrigerator, 10 - hydrocarbon reactor, 11 - fraction collector, 12 - system pressure regulator, 13 - nitrogen cylinder, 14 - chromatograph.

2.3 Ammonia chemosorption study

To determine the number and strength of Brønsted acid sites located on the surface of initial H-ZSM-5 sample and catalysts after reaction, thermoprogrammed desorption of ammonia was carried out on a Chemosorb 4580 gas chemisorption analyzer (Micrometrics, USA). For the analysis, 0.4 g of the catalyst was placed in a quartz cuvette and purged with helium at a rate of 50 ml/min and heated to 550°C at a rate of 50°C/min, after which it was kept at this temperature for one hour, and sample was cooled to 100°C. After cooling, the sample was purged with a mixture of ammonia in helium of 10 vol. % for one hour. After which, the sample was blown with helium for an hour, respectively. The sample was heated up to 550°C at a rate of 50°C/min and ammonia desorption profile was recorded. The amount of desorbed ammonia was determined using a katharometer and previously calculated calibration curves. The amount of ammonia was converted to the number of surface acid sites.

3. Results and discussions

Deactivation of zeolites in kinetic models is a rather complicated problem associated with the high complicity of the deactivation mechanism. Typically for the determination of deactivation kinetics (Schipper and Krambeck, 1986) additional coefficient β is introduced reaction kinetics curves by which the rate of reactions for the initial catalyst (1) is multiplied.

$$r_i = r_{i0} - \beta\tau \tag{1}$$

Where r_i is the actual process rate, r_{i0} is the process rate for the original catalyst, β is the catalyst deactivation factor, τ – time on stream, h or quantity of transformed DME, kg(DME)/kg(Cat).

For taking into account irreversible catalyst deactivation aquation (1) can be modified in function (2).

$$r_i = r_{i0}\alpha^n - \beta\tau \tag{2}$$

Where α is the factor of catalyst irreversible deactivation, n – quantity of catalyst regenerations, times.
For the stage of DME to hydrocarbons transformation (Figure 2 a, b) it is possible to apply these aquations in case of linear kinetic curve behavior, which is applicable for the first part of the reaction (180-200 hours on stream or 35-40 kg(DME)/kg(Cat).
Numerical determination of α and β coefficient for Figure 2b in MatLab software using Levenberg-Marquardt algorithm allows to get values α=0.82 and β=0.0015 1/h average approximation accuracy was 0.87, relative errors at high values of DME consumption exceed 20% (Figure 2a).

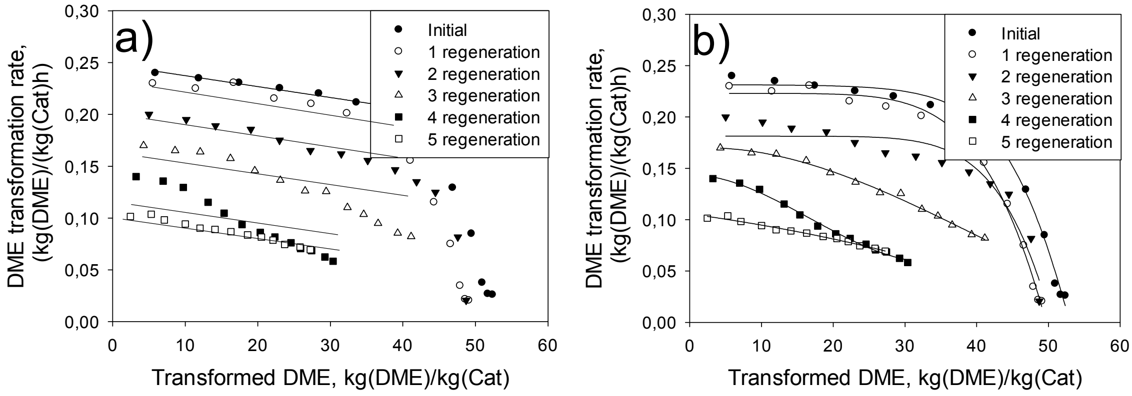


*Figure 2. Comparison of model lines and experimental plots for dimethyl ether (DME) transformation rate quantity of transformed dimethyl ether for a) simple model according to aquations (1-2), b – modified model with equations (3-4):(weight hourly space velocity of methanol – 0.7 kg(Me)/(kg(Cat)*h)), t=350 °C).*

However, such an approach, not taking in account reaction mechanism, is applicable for large-scale industrial systems, where the quantity of influencing factors is very large. For considering of reaction mechanism and evaluation of catalyst deactivation at high values of consumed reagent it is possible to apply additional aquation (3-4) to determine α and β change during the reaction.

$$\frac{d\alpha}{dt} = k_\alpha \alpha^m \tag{3}$$

$$\frac{d\beta}{dt} = k_\beta \beta^b \tag{4}$$

Where α is the factor of catalyst irreversible deactivation, β is the catalyst reversible deactivation factor, k_β – reaction constant of carbon deposition on the catalyst surface, k_α – reaction constant of active sites hydrolysis b – reaction order of carbon surface deposition on catalysts, m – reaction order of active cites hydrolysis.
Numerical joint solution of equations (9-11) for deactivation of H-ZSM-5 zeolite during reaction (Figure 2b) allows to determine $k_\alpha = 14831$/h, $k_\beta = 7819\ 1/h$ deactivation rate constants, factors of deactivation α=0.85, β=0.0011 1/h and reaction orders b=1.4, m=0.9 relative error of determined constants 15%. However, the presented approach has a lack correlation with possible deactivation mechanism.

Typically, the methanol transformation reaction scheme contains a hydrocarbon pool consist of a reaction cycle for light olefins (I) and aromatic (II) formation (Figure 3), while for evaluation of catalyst deactivation kinetics, an additional reaction cycle containing polyaromatic compounds (III) should be added.

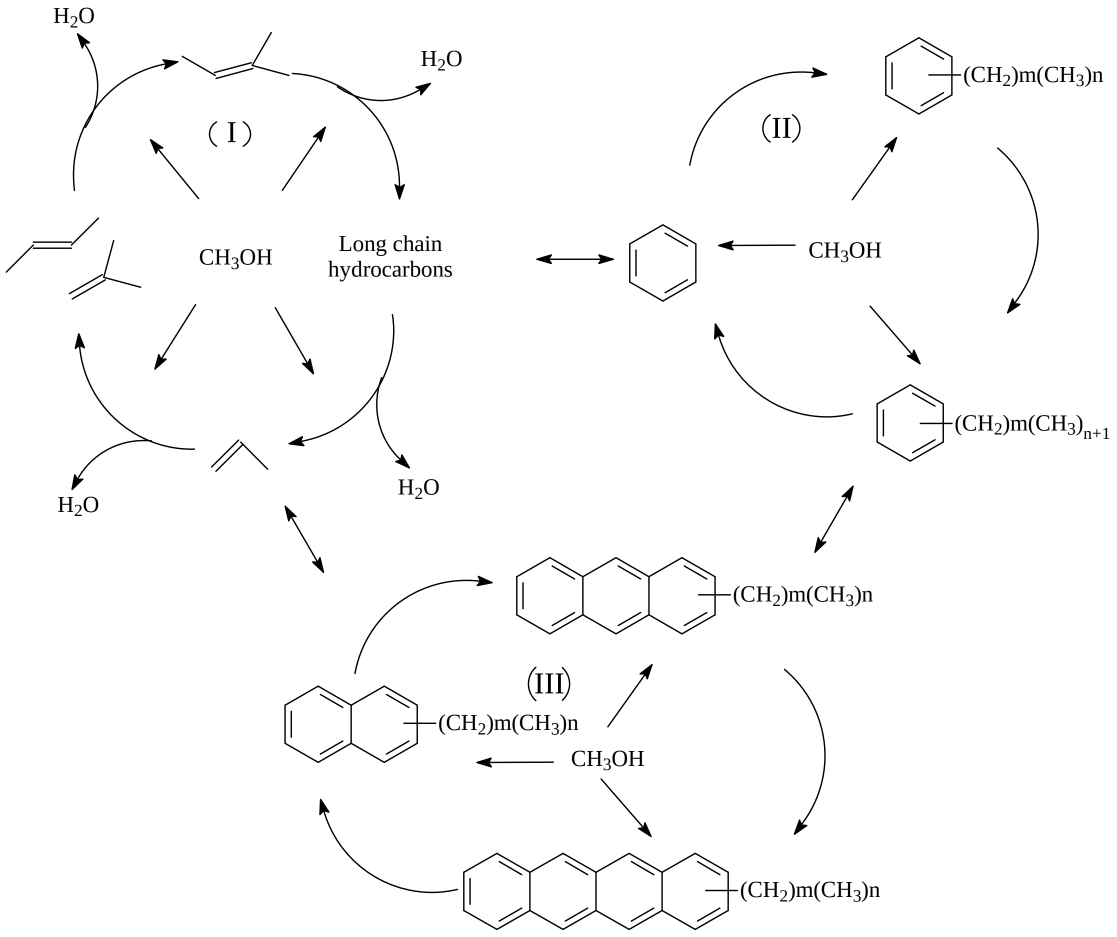
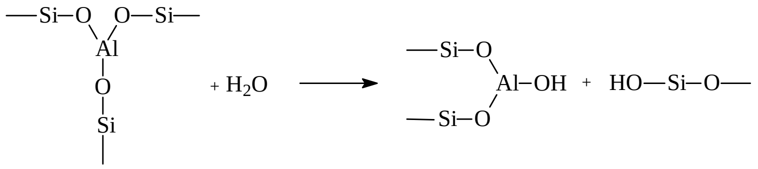
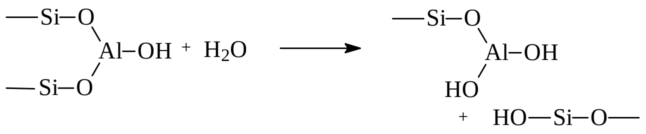


Figure 3: Reaction scheme of methanol to hydrocarbons transformation process

Degradation of Brønsted acid sites during steam treatment taking place in methanol to hydrocarbons transformation reaction can be expressed by equations 5-7, where the first two stages can be considered as reversible or at least partly reversible. In the case of catalyst calcination, surface dehydration takes place. Therefore, zeolite activity can be partially restored.



(5)



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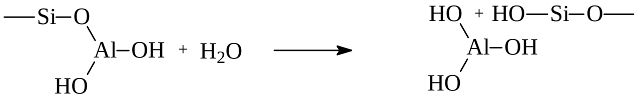

(7)

The last stage of the interaction of Brønsted acid sites with water leads to irreversible hydrolysis of the active site and the formation of amorphous aluminum hydroxide, which can be washed out during the reaction or form a separate phase of alumina upon calcination. In any case, the sequential reaction during three stages of stepwise hydrolysis of the active sites results in it completely destroy and, as a consequence, the activity of the catalyst decreases irreversibly. Based on the above chemical reactions (5-7) and strong adsorption of polyaromatic compounds, it is possible to write down the scheme of steam and heavy polyaromatics deactivation of the active sites of zeolite (12-15).

$$\Theta_{as}+H_2O \leftrightarrow \Theta_{as}\times H_2O \tag{12}$$

$$\Theta_{as}\times H_2O+H_2O \leftrightarrow \Theta_{as}\times 2H_2O \tag{13}$$

$$\Theta_{as}\times 2H_2O+H_2O \rightarrow \Theta_{as}\times 3H_2O \tag{14}$$

$$\Theta_{as}+C^{14+} \leftrightarrow \Theta_{as}\times C \tag{15}$$

Where Θ_{as} is surface coverage with free active sites, $\Theta_{as}\times H_2O$ - is surface coverage with mono hydrated active sites, $\Theta_{as}\times 2H_2O$ - is surface coverage with bi hydrated active sites, $\Theta_{as}\times 3H_2O$ - is surface coverage with mono hydrated active sites, $\Theta_{as}\times C$ - is surface coverage with active sites with adsorbed heavy polyaromatics.

Overall decrease of active sites surface concentration during the reaction can be calculated according to equation (16), and irreversible reduction of active sites surface concentration can be calculated by equation (17). For calculation of active sites, water partial pressure and polyaromatic lump with carbon atoms numbers equal or higher than 14 (C14+ - anthracene, phenanthrene etc.) was taken, partial pressures were evaluated according to chromatography data taking in to account fugacity of the substances.

$$\frac{dC_{as}}{dt} = -C_{as}(k_{12}p(H_2O) + k_{15}p(C^{14+})) \tag{16}$$

$$\frac{dC_{as\,\mathrm{irr.}}}{dt} = C_{as}\frac{-k_{14}K_{12}K_{13}p_{H_2O}^{3}(1-\Theta_{\mathrm{as}\times 2H_2O}-\Theta_{\mathrm{as}\times 3H_2O}-\Theta_{\mathrm{as}\times C})}{1+K_{12}p(H_2O)} \tag{17}$$

Reaction rate of DME to hydrocarbons transformation can be calculated due to equation 18, considering process chemistry and Eley–Rideal mechanism.

$$r_{DME} = C_{as}\sum k\frac{p(Prod)p(CH_3OCH_3)}{1+\mathrm{K}p(Prod)} \tag{18}$$

Where C_{as} is quantity of active sites, mol/kg, $p(Prod)$ – partial pressure of the products, $p(CH_3OCH_3)$ – partial pressure of DME, K - adsorption constants according to the reaction chemistry.

Solution of equations (16-17), considering concentration of active sites measured by ammonia chemosorption, water partial pressure and polyaromatics partial pressure allows to determine k_{12}=834 1/h, k_{14}=1274 1/h, k_{15}=5978 1/h and K_{12}=1394, K_{13}=2426 relative errors of determined constants were lower than 10%.

4. Conclusions

Zeolite deactivation particularities in the methanol to hydrocarbons transformation process were discussed. Three deactivation models were studied and applied to show their advantages and disadvantages. The simple linear deactivation model showed the possibility of its usage only in the first parts of the deactivation process, where kinetic curves were linear. However, in the second part of the reaction, kinetic curves had exponential character. Therefore, the application of the linear model was inadequate. An operator addition to a simple linear model for determination of deactivation rate change allowed to improve model reliability. Nevertheless, model remains relatively simple for calculation, but both models have a low correlation with the reaction mechanism. To improve this additional model was developed using chemical equations for catalysts surface deactivation. This model is characterized by close interaction with possible reaction mechanisms, but additional data on active sites quantity on the catalyst surface was needed to provide calculations. The application of this model allows improving results accuracy.

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