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# *A review on kinetic modeling of deactivation of SAPO-34 catalyst during Methanol to Olefins (MTO) process*

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*Una revisión de los modelos cinéticos de la desactivación del catalizador SAPO-34 durante el proceso Metanol a Olefinas (MTO)*

*Una revisió dels models cinètics de la desactivació del catalitzador SAPO-34 durant el procés Metanol a Olefines (MTO)*

*Recibido: 29 de abril de 2013; revisado: 18 de febrero de 2013; aceptado: 15 de marzo de 2013*

## RESUMEN

La causa principal de desactivación en la reacción de MTO sobre SAPO-34 es la deposición de coque que influye tanto la actividad como la selectividad. Esta revisión describe diferentes modelos cinéticos de desactivación de SAPO-34 durante el proceso MTO. También se presentan distintas funciones de desactivación para la conversión de metanol y para el rendimiento en olefinas, las cuales son hiperbólicas y exponenciales respectivamente. Un modelo de Voorhies que estima la selectividad promedio del coque y la capacidad catalítica para la formación de olefinas, describe una buena relación entre la deposición de coque y la cantidad de hidrocarburos formados por gramo de catalizador. Se presenta la relación entre el contenido de coque frente a SAPO-34 y la cantidad acumulada de metanol añadido a los catalizadores, para estimar el contenido de coque en SAPO-34 en distintas condiciones de reacción. Además, se han simulado los cambios en actividad y selectividad con el contenido de coque mediante un modelo cinético que incluye el efecto de desactivación.

**Palabras clave:** deposición de coque, desactivación, modelización cinética, reacción MTO, SAPO-34

## SUMMARY

The major cause of deactivation in the MTO reaction over SAPO-34 is coke deposition that influences both activity and selectivity. This review describes different kinetic modeling of deactivation of SAPO-34 during MTO process. It also presents different deactivation functions for the methanol conversion and the yields of olefins, which are hyperbolic and exponential respectively. A modified Voorhies model that estimates the average coke selectivity and catalyst capacity for olefin formation describes a good relation between coke deposition and the amount of hydrocarbons formed per gram of catalyst.

Relation between the coke content over SAPO-34 and cumulative amount of methanol fed to the catalysts is presented to estimate the coke content on SAPO-34 at different reaction conditions. In addition, the changes in activity and selectivity with the coke content are simulated by a kinetic model, which includes the deactivation effect.

**Key words:** coke deposition, deactivation, kinetic modeling, MTO reaction, SAPO-34

## RESUM

La causa principal de desactivació en la reacció MTO sobre SAPO-34 és la deposició de coc que influeix tant l'activitat com la selectivitat. Aquesta revisió descriu diferents models cinètics de desactivació de SAPO-34 durant el procés MTO. També es presenten diferents funcions de desactivació per a la conversió de metanol i per el rendiment en olefines, que són hiperbòliques i exponencials respectivament. Un model de Voorhies que estima la selectivitat mitjana del coc i la capacitat catalítica per a la formació d'olefina, descriu una bona relació entre la deposició de coc i la quantitat d'hidrocarburs formats per gram de catalitzador. Es presenta la relació entre el contingut de coc enfront de SAPO-34 i la quantitat acumulada de metanol afegit als catalitzadors, per estimar el contingut de coc en SAPO-34 en diferents condicions de reacció. A més, s'han simulat els canvis en activitat i selectivitat amb el contingut de coc, mitjançant un model cinètic que inclou l'efecte de desactivació.

**Paraules clau:** deposició de coc, desactivació, modelització cinètica, reacció MTO, SAPO-34

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## INTRODUCTION

Methanol to olefins (MTO) joined with transformation of coal or natural gas to methanol gives a fascinating way to produce ethylene and propylene. This process has been investigated thoroughly both from the economic and scientific viewpoint [1–5].

The catalytic conversion of methanol to olefins (MTO) was originally an intermediate step in Mobil's process to convert methanol to synthetic gasoline using HZSM-5 as catalyst. However, interest has recently shifted toward the MTO process following the increased demand for olefins. The oil crisis in 20th century accelerated this study, which was proved a feasible way to obtain light olefins, particularly ethylene and propylene, from non-petroleum feedstock.

The methanol-to-olefin (MTO) process successfully produces lower olefins, the most important raw materials of the petrochemical industry, from various non-petroleum sources such as natural gas, coal and biomass [1–3].

Although the mechanism of the MTO reaction is very simple, following the pathway of methanol (MeOH)→dimethylether (DME)→lower olefins, various reaction intermediates have been suggested to explain the carbon-carbon bond formation from MeOH.

There are many molecular sieve catalysts, such as ZSM-5 [6–8], modified Y [9], mordenite [10], chabazite [11], and others [12–14], that could be used in the conversion of methanol to olefins. However, SAPO-34, among other catalysts, shows the best performance in terms of activity and selectivity to light olefins, which could achieve 100% methanol conversion and 90% selectivity to light olefins while no C<sub>6+</sub> hydrocarbons have been generated [15]. The characteristics of SAPO-34 or its modification and its applications in the MTO process have been described elsewhere [5,13–16]. On the other hand, SAPO-34, as a micropores zeolitic material, is known to suffer rapid deactivation by coking in the MTO process which influences both activity and selectivity [13,17–20].

Most kinetic studies on methanol conversion have been made on HZSM-5 catalysts, and a number of simplified kinetic models have been developed. Catalytic processes using zeolites often include side reactions, leading to the formation of carbonaceous material with catalyst deactivation as a result. Zeolite type catalysts are used widely in petrochemical and petroleum refining processes [21].

SAPO-34 catalyst with interconnecting three-dimensional network of pores with supercages provides room for accommodating some coke without immediate blocking of the pores [5]. Aromatics and branched isomers form inside the cavities and adsorb irreversibly on strong acid sites, which result in a decrease in concentration of strong acid sites.

The catalytic conversion of methanol to lower olefins (MTO) is an interesting and promising way of converting natural gas and coal to chemicals via methanol [22, 23]. Coke deposition is known to be the major cause of deactivation in the MTO reaction over SAPO-34, and both activity and selectivity are influenced by coke deposition [24–28].

The modeling of coke deposition and deactivation was reviewed by Froment in 1976 [29] and 1991 [30]. Earlier work was aimed at relating the coke deposition, as well as the deactivation, empirically to the time on stream based on the observation that coke formation was not dependent on the space velocity [31]. This might not be valid for different

feeds and catalysts. However, Voorhies' rate law has been widely accepted [32,33].

Fast deactivation of the catalyst due to coke formation has been reported. [34–36]. Most kinetic studies on methanol conversion have been made on HZSM-5 catalysts, and a number of simplified kinetic models have been developed. The complexity of the model varies according to the degree of lumping proposed.[37–41] A very detailed analysis has been performed by Mihail et al.[42,43] in which 33 reactions were used. Single-event kinetic modeling of MTO on H-ZSM-5 has been performed by Park and Froment [44,45] on the basis of a detailed mechanistic description of the MTO reaction.

Deactivation by coking may be due to both coverage of acid sites and blockage of the pore structure [5,46,47]. Marchi and Froment [13] suggested that the deactivation by coke and its effect on product distribution depend on the way the coke is deposited on the catalyst. With the increasing coke deposition on the catalyst, the pores are blocked and the concentration of acid sites decays abruptly, and so do the methanol conversion and the yields of various products [5,13]. Most workers [13,17–20,48,49] proved that even though the catalyst suffers a serious coke deposition, the methanol conversion, unlike the yields of olefins, does not drop to zero because of the occurrence of the reaction of methanol to dimethyl ether (DME) over relatively weak acid sites.

In this paper, some kinetic modeling of deactivation of SAPO-34 during MTO process is studied. The first work deals with the behaviors of coke deposition over SAPO-34 catalyst and a model for coke formation is proposed. The obtained information of coke formation is useful to select suitable operating condition and minimize the unfavorable effect of coking on the catalyst or products selectivity.

The second work deals with the detailed study of coke formation as a function of operating conditions such as space velocity, temperature and partial pressure of methanol. Models for coke formation are proposed starting from the simple modified Voorhies model and proceeding to a more elaborate model.

In third work, the deactivation of SAPO-34 is modeled based upon the elementary steps and the single event concept. The model was then utilized to introduce the deactivation of the catalyst into the kinetic equations for the purpose of simulation of reactor behavior.

The fourth work will focus on the selectivity to olefins and its changes with coke formation. A reaction network is proposed, and a kinetic model for this reaction network is developed, including the deactivation due to coke deposition.

### 1. SAPO-34 deactivation models

#### 1.1. Behaviors of coke deposition on SAPO-34 catalyst during methanol conversion to light olefins by Guozhen Qi et al.

The reaction has been accomplished in an isothermal fixed-bed integral reactor under the following conditions: a total pressure of 100 kPa, temperatures between 623 and 823 K range, contact times of 0.02 and 0.12 h<sup>-1</sup>, catalyst particle sizes of 0.4–0.8 mm. The catalyst is diluted to 20 wt. % with quartz of 0.4–0.8 mm to obtain bed isothermality (the MTO process is generously exothermic, almost 20–30 kJ mol<sup>-1</sup>).

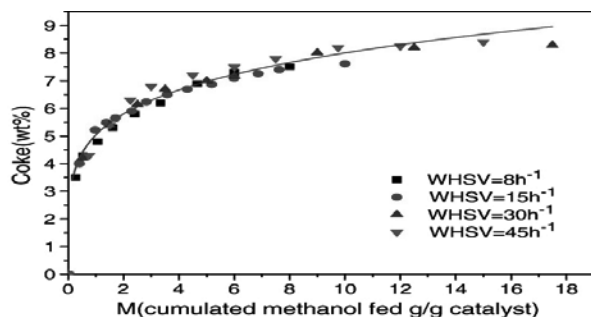
**Table 1.** Parameters in Eq. (1) for MTO over SAPO-34 at different temperatures. Adapted with permission from [50].

Temperature (K)	$\alpha$	b
623	4.25	0.13
673	4.68	0.12
723	5.22	0.14
743	5.51	0.15
773	6.15	0.15
823	7.13	0.14

The amount of coke on the SAPO-34 catalyst with time on stream (TOS) at different reaction temperatures is shown in experimental data [50]. It can be observed that the higher temperature the higher coke formation, which means that high temperature prefers coke formation. The higher coke deposition rate during MTO reaction may be due to the special pore structure of SAPO-34 catalyst, SAPO-34 has small size channels and intersections between the channels that give way to cavities whose size allows arrangement of high molecular weight structures.

The amount of coke on the SAPO-34 catalyst for feeds versus different water contents is available [50]. When the coke deposition over SAPO-34 catalyst becomes filled to capacity, the amount of coke deposition stays almost constant and the influence of water content in feed on the coke content cannot be observed.

Voorhies [51] suggested a kinetic model that connects coke formation to time on stream for oil racking on silica-alumina, and for other reaction systems it has valid [52,53]. Chen et al. [17] and Benito et al. [54] proved that the coke deposition is influenced by the reaction conditions containing space velocity, methanol partial pressure and temperature in MTO reaction over SAPO-34. As shown in Fig. 1, the coke deposition during the MTO reaction over SAPO-34 at constant temperature mainly relies upon the cumulative amount of methanol fed to the catalysts (M).



**Fig. 1.** Coke content over SAPO-34 vs. cumulative amount of methanol fed to the catalysts (M) at 723 K in different methanol weight hourly space velocities (WHSV). Adapted with permission from [50].

Therefore, the Voorhies model of coke formation can be modified by:

$$C_c = \alpha \cdot M^b \quad (1)$$

Where a and b are listed in Table 1 for different temperatures that they are parameters only rely upon the temperature and must be estimated. In practice, it is difficult to evaluate the amount of coke. Hence, Eq. (1) estimate the amount of coke on SAPO-34 based on the cumulative amount of methanol fed to the catalysts (M) at different reaction conditions.

## 1.2. Methanol conversion to light olefins over SAPO-34: kinetic modeling of coke formation by Chen et al.

The MTO reaction was carried out at a WHSV ranging from 57 to 385 g/g<sub>cat</sub> h, a methanol partial pressure ranging from 7.2 to 83 kPa, and temperatures between 673 and 823 K. The runs were performed with different space velocities at 698 K and a methanol partial pressure of 7.2 kPa, to acquire comparatively low coking rate. The runs with different methanol partial pressures were also carried out at 698 K. The reactor effluent containing unconverted MeOH and dimethylether (DME) was analyzed on either on an HP 5890 or an HP 6890 gas chromatograph. The experimental procedures, the TEOM reactor and the catalyst properties were depicted [55,56].

Some definitions used in the discussion are illustrated in the following:

- Cumulative amount of methanol fed to the catalysts (CAMF) =  $t \times \text{WHSV}$  (g/g cat).
- Cumulative amount of methanol fed to the catalysts (CAMF, CH<sub>2</sub> basis) =  $\text{CAMF} \times 14/32$ .
- Cumulative amount of hydrocarbon formed (CAHF) (g/gcat) =  $\int_0^{\text{CAMF}} X \, d(\text{CAMF})$ .
- For 3 min pulses CAHF is approximately  $\text{CAHF} = \sum_j X_j (3/60)$  WHSV, where j is the number of pulses.
- Catalyst capacity ( $g_{\text{hydrocarbon}}/g_{\text{cat}}$ ) = amount of hydrocarbon formed per gram of catalyst until a certain loss in catalyst activity.
- Average coke selectivity (wt %) = the ratio of the coke content to the amount of hydrocarbon formed.
- The amount of coke on the catalyst is given as g of coke/100 g of dry, coke-free catalyst.

In this series of experiments, four effects that influence the coke deposition and deactivation rates were investigated by using different parameters such as pulse lengths, catalyst loading, etc [57].

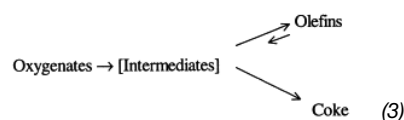
The effect of stripping in helium could influence the nature of the coke or the location of the coke but it was found that stripping in helium did not significantly influence the coke deposition and the deactivation. Experiments demonstrate that the coke deposition depends on the space velocity. Lower space velocities gave higher coking rate. The change in conversion with CAMF can be described by:

$$X = X_0 \exp(-\alpha \text{CAMF}) \quad (2)$$

Both the conversion X and CAMF in Eq. (2) are on a CH<sub>2</sub> basis. The initial conversion X<sub>0</sub> and the constant  $\alpha$  were determined by curve fitting.

The third effect is partial pressure of methanol. Preliminary experiments showed that the conversion and the coke deposition increased with increasing partial pressure of methanol. but the fact is that the coke deposition was almost identical for the different experiments implies that coke deposition can be directly related to the total amount of hydrocarbons formed during the reaction, regardless of the methanol partial pressure. The last effect is temperature. The average coke selectivity increases with temperature, means the higher temperatures the higher coke-forming reaction.

A simple mechanism of coke deposition can be proposed:



Where the oxygenates consist methanol and dimethylether, and all hydrocarbons are lumped together based on the observation that the olefins are formed from the oxygenates in parallel [58]. The intermediates are a mixture of carbenium ions with different carbon numbers inside the pores. This simple mechanism for coke formation is similar to the hydrocarbon pool mechanism [59,60].

In the present work, two models are given and discussed as follows:

Model I:

The modified Voorhies coking model can be described by:

$$C \text{ (wt \%)} = a [\text{CAHF}]^b \quad (4)$$

Where  $a$  and  $b$  are parameters to be estimated and their values are presented in Table 2 for different temperatures.  $a$  and  $b$  did only depend on the temperature.

The instantaneous coke selectivity ( $S_c$ , wt %), that is a useful value for understanding of the effects of coke deposition on the coking and olefin formation inside the pores, can be calculated by derivation of Eq. (4) :

$$S_c = \frac{dC}{d \text{CAHF}} = ab [\text{CAHF}]^{b-1} \quad (5)$$

The average coke selectivity ( $S_{av,C}$ , wt %) is a useful parameter for catalyst evaluation. From Eq. (4), the coke selectivity can be expressed as:

$$S_{av,C} \text{ (wt\%)} = \frac{C}{[\text{CAHF}]} = a^{1/b} C^{1-1/b} \quad (6)$$

**Table 2.** Parameters in Model I ( $C \text{ (wt \%)} = a [\text{CAHF}]^b$ ) for MTO over SAPO-34 at different temperatures. Adapted with permission from [57].

Temperature (K.)	$a$	$b$
673	1.09	0.83
698	2.09	0.80
773	1.71	1.08
823	3.24	1.23

In any way, Voorhies' relationship ignores the coking reaction itself therefore provides little information about the mechanism of coke deposition.

#### Model II :

Since Model I [Eq. (4)] has the restrictions. A proper kinetic model should explain all the experimental observations, such as the changes in the coke content versus the cumulative amount of methanol fed to the catalyst ( $m^2$ ). The conventional model of Froment and Bischoff [61] relates the coking rate ( $dC/dt$ ) to the concentration of coke precursor and the deactivation function of the coking reaction:

$$\frac{dC}{d \text{CAHF}} = k_c^0 (C^*)^n \phi_C \quad (7)$$

Where  $k_c^0$  is the initial coking rate constant,  $n$  is the reaction order and  $\phi_C$  is the deactivation function for the coking reactions.  $C^*$  is the concentration of the coke precursor, which is assumed to be proportional to the conversion of oxygenates ( $C^* = X_{oxy} C_{A0}$ ,  $C_{A0}$  being the initial concentration of methanol and  $X_{oxy}$  being the oxygenate conversion). However, the residence time in the reactor is in the range of milliseconds. Since no appreciable deactivation occurs over a time period of milliseconds, the process can be treated as pseudo steady-state. The mass balance for the  $i$ th CSTR in the series is:

$$\Delta x_i = \Delta (W/F_{A0}) r_{A,i} / \tau_S \quad (8)$$

$$r_{A,i} = k_{oxy}^0 \phi_{oxy} C_{A,i} \quad (9)$$

$\Delta x_i$  is the conversion of oxygenates in the  $i$ th CSTR, which can be written as:

$$\Delta x_i = 1 - 1 / (1 + \Delta (W/F_{A0}) / \rho_S C_{Ain,i} k_{oxy}^0 \phi_{oxy}) \quad (10)$$

And

$$C_{Ain,i} = C_{Ain,i-1} (1 - \Delta x_{i-1}) \quad (11)$$

$C_{Ain,i}$  is the inlet concentration of  $i$ th CSTR.

$$X_i = \frac{C_{A0} - C_{Ain,i}}{C_{A0}} \quad (12)$$

The coking rate in  $i$ th CSTR is:

$$\frac{dC_i}{dt} = r_{C,i}^0 \phi_C \quad (13)$$

The initial coking rate in the  $i$ th CSTR ( $r_{C,i}^0$ ) is a function of the conversion of oxygenates and the reactant to catalyst ratio (RTC,  $g_{feed}/g_{cat}$ ). The initial coking rate is then illustrated by:

$$r_{C,i}^0 = k_C^0 \text{RTC} \Delta x_i \quad (14)$$

Eq. (14) is rewritten in the form of:

$$r_{C,i}^0 = k_C^0 \Delta x_i / t_i \quad (15)$$

Where the space time  $t_i$  in  $i$ th CSTR is defined as  $t_i = (\Delta \text{WHSV})^{-1} (g_{cat} h / g_{feed})$ . It must be mentioned that  $k_C^0$  in Eq. (15) is not identical to in Eq. (14).

Eq. (16) shows a linear relationship between the degree of deactivation and the coke content and gives the best fit for both the MTO reaction and the coke deposition:

$$\phi_{oxy} = 1 - \alpha_{oxy} C \quad \text{and} \quad \phi_C = 1 - \alpha_C C. \quad (16)$$

Integration of the continuity equation [Eq. (13)] combined with Eqs. (15) and (16) yields:

$$C_i = \frac{1}{\alpha_C} \left[ 1 - \exp \left( -\alpha_C k_C^0 \frac{t}{\tau_i} \Delta x_i \right) \right] \quad (17)$$

Where  $t/\tau_i = \Delta (\text{CAMF}) (g_{MeOH}/g_{cat})$ . This equation is in good agreement with the experimental data.

In the kinetic model with using the Levenberg-Marquardt method [62], the estimation of the parameters has been performed by the non-linear least squares routine in MATLAB. The objective function OF was calculated:

$$\text{OF} = \sum_{j=1}^n \left( \frac{X_j^{\text{exp}} - X_j^{\text{cal}}}{X_j^{\text{exp}}} \right)^2 + \sum_{j=1}^n \left( \frac{C_{av,j}^{\text{exp}} - C_{av,j}^{\text{cal}}}{C_j^{\text{exp}}} \right)^2 \quad (18)$$

Where  $X_{j,N}^{\text{cal}}$  are the calculated values of the total conversion of the oxygenates at a given coke content and at the experimental point  $j$ .  $X_j^{\text{exp}}$  are the corresponding experimental values.  $C_{av,j}^{\text{cal}}$  are the calculated average coke content at the experimental point  $j$ , which is calculated by Eq. (19) and  $C_j^{\text{exp}}$  is the corresponding experimental value. Due to the large variation in conversion and coke content in the

experiments,  $1/X_j^{\text{exp}}$  and  $1/C_j^{\text{exp}}$  are used as the weighting factors:

$$C_{\text{av}} = \left( \sum_{i=1}^N C_i \right) / N \quad (19)$$

$N=20$  was chosen. The estimated parameters are displayed in Table 3.  $k_C^0$  and  $k_{\text{oxy}}^0$  are depended to the temperature. The data fitted the Arrhenius correlations well:

$$k_{\text{oxy}}^0 = 3.96 \times 10^{12} \exp(-117735/8.314T), \gamma^2 = 0.9897 \quad (20)$$

$$k_C^0 = 1.27 \exp(-6707/8.314T), \gamma^2 = 0.9968 \quad (21)$$

Table 3. Parameters in Model II for MTO over SAPO-34 at different Temperatures. Adapted with permission from [57].

Temperature (K)	$k_C^0$	$\alpha_C$	$k_{\text{oxy}}^0$ ( $s^{-1}$ )	$\alpha_{\text{oxy}}$
673	0.33	0.061	2684	0.043
698	0.40	0.058	7235	0.052
773	0.45	0.035	35 132	0.057
823	0.48	0.033	150941	0.070

#### Nomenclature

a	empirical constant in the modified Voorhies model
b	empirical constant in the modified Voorhies model
CAHF	cumulative amount of hydrocarbons formed per gram of catalyst ( $g/g_{\text{cat}}$ )
C	coke content ( $g_{\text{coke}}/100 g_{\text{cat}}$ , dry)
$C_i$	coke content in the ith CSTR
$C_j^{\text{exp}}$	experimental coke content at the jth experiment
$C_{\text{av},j}^{\text{cal}}$	calculated average coke content at the jth experiment
$C^*$	concentration of the coke precursor
$C_{A0}$	initial concentration of oxygenates
$C_{A,i}$	concentration of oxygenates in the ith CSTR
$C_{\text{Ain},i}$	inlet concentration of oxygenates to the ith CSTR
CAMF	cumulative amount of methanol fed to the catalyst ( $g_{\text{MeOH}}/g_{\text{cat}}$ )
$F_{A0}$	molar flow rate of MeOH (mol/h)
$k_{\text{oxy}}^0$	initial reaction rate constant of oxygenates ( $s^{-1}$ )
$k_C^0$	initial rate constant for coke formation
m	number of experiments
N	number of CSTRs used in the model
n	reaction order
OF	objective function
$r_{\text{oxy}}^0$	initial rate of oxygenates conversion, on a CH <sub>2</sub> basis ( $kmol/kg_{\text{cat}} \cdot s$ )
$r_C^0$	initial rate of coke formation ( $kg_{\text{coke}}/kg_{\text{cat}} \cdot h$ )
RTC	reactant to catalyst ratio
$S_{\text{av},C}$	average coke selectivity (wt%)
$S_C$	instantaneous coke selectivity (wt%)
T	reaction temperature (K)
t	time on stream (h)
W	catalyst loading ( $g_{\text{cat}}$ )
WHSV	weight hourly space velocity (on a methanol basis) ( $kg_{\text{MeOH}}/kg_{\text{cat}} \cdot h$ )
$X_i$	conversion of oxygenates until the ith CSTR, CH <sub>2</sub> basis
$X_j^{\text{exp}}$	experimental total conversion of oxygenates, CH <sub>2</sub> basis
$X_{j,N}^{\text{cal}}$	calculated total conversion of oxygenates, CH <sub>2</sub> basis
$\Delta x_i$	concentration of oxygenates in the ith CSTR

$\alpha$	empirical deactivation constant defined by Eq. (2)
$\gamma^2$	R-squared value
$\rho_s$	catalyst density ( $kg_{\text{cat}}/m^3$ )
$t_i$	space time in the ith CSTR ( $kg_{\text{cat}} \cdot h/kg_{\text{MeOH}}$ )
$\Phi_C$	deactivation function for the coke formation
$\Phi_{\text{oxy}}$	deactivation function for the conversion of Oxygenates

#### 1.3 Conversion of methanol to light olefins over SAPO-34: kinetic modeling and catalyst deactivation by Saeed M. Al Wahabi.

The rapid deactivation of SAPO-34 was ascribed to both coverage of the acid sites and blockage of pore structure [63]. A typical deactivation behavior of a SAPO-34 catalyst was depicted in [64], as measured by Marchi and Froment [65].

It illustrates that the deactivation functions for the methanol conversion and the yields of olefins are different. The function for the methanol conversion to DME is a hyperbolic that does not drop to zero and for the olefins is exponential and drops to zero. In this work, modeling of catalyst deactivation is based upon the elementary steps and the single event concept.

The deactivation is occurred when higher oligomerization products (C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>) permanently cover the acid active sites and block pores. The C<sub>6+</sub> products rate of formation and concentration inside the cages can be calculated as follow:

Evans-Polanyi relationship can be used to calculate the activation energies of C<sub>6+</sub> formation and cracking. The frequency factor for the formation of C<sub>4</sub> and C<sub>5</sub> can be used to calculate the rate of formation of the C<sub>6+</sub> components. The heats of protonation  $\Delta H_{\text{Pr}}(O_{ir})$  for the reference olefins of different carbon can be obtained for SAPO-34 up to C<sub>5</sub> olefins with those of ZSM-5 estimated by Park [66]. The concentration of the C<sub>6+</sub> components develops with time in accord with:

$$\frac{dC_{C6+}}{dt} = \Phi_C \cdot r_C \quad (22)$$

With initial condition,

$$\text{At } t=0 \quad C_{C6+}=0 \quad \text{for all } \frac{W}{F_{\text{MeOH}}}$$

$$\text{Where } r_C = \sum_{i=6}^8 M_i R_i$$

$M_i$  = Molecular weight of component i.

$R_i$  = Net rate of formation of component i in (moles/ $g_{\text{cat}} \cdot h$ ).

$\Phi_C$  is the deactivation function and it is expressed by Froment and Bischoff [67] as follows:

$$\Phi_C = \exp(-\alpha C_{C6+}) \quad (23)$$

Equation (22) is integrated simultaneously with the set of continuity equations describing the behavior of methanol and the various reaction products in the reactor:

$$\frac{d\Phi_i}{d(W/F_{\text{MeOH}})} = \frac{100 \cdot M_i}{M_{\text{MeOH}}} \cdot \Phi_i \cdot R_i, \quad i=1,2,\dots,m \quad (24)$$

Where  $\Phi_i$  are the deactivation functions for the main reactions expressed as follows:

$$\Phi_i = \exp(-\alpha C_{C6+}) \quad \text{for olefins formation} \quad (25)$$

$$\Phi_i = \frac{1}{1 + \beta C_{C6+}} \quad \text{for methanol conversion} \quad (26)$$

Two unknown parameters  $\alpha$  and  $\beta$  are estimated by the experimental data of Marchi and Froment [65]. It can be obtained from the comparison of methanol conversion and C2-C4 olefins yield determined by the model with the experimental data [64]:

- MeOH conversion remains constant for some time before deactivation breakthrough.
- The amount of catalyst and the water content of the feed affect on the breakthrough point.

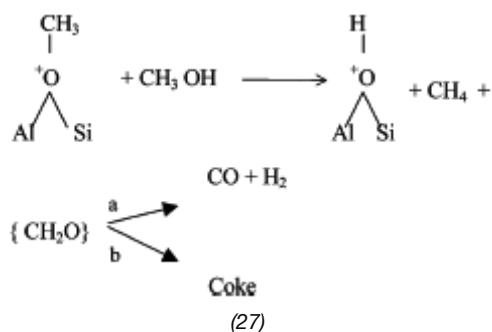
This paper illustrates the manner of acting of the MeOH conversion inside the reactor in the presence of deactivation and the concentration of the C6+ olefins.

When the breakthrough point is reached, the deactivation is observed at the exit of the reactor and also near the inlet of the reactor, the C6+ olefins are reached a maximum because of rapid production with simultaneous decomposition by beta scission.

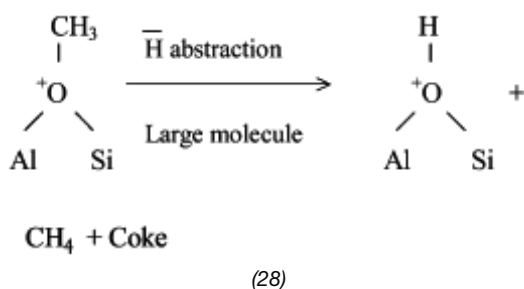
#### 1.4. Methanol conversion to light olefins over SAPO-34: Reaction Network and Deactivation Kinetics by Chen et al.

The MTO reaction was carried out at a WHSV ranging from 57 to 2558 g/g<sub>cat</sub> h, a methanol partial pressure ranging from 7.2 to 83 kPa, and temperatures between 673 and 823 K. The runs were performed with different space velocities at 698 K and a methanol partial pressure of 7.2 kPa, to acquire comparatively low coking rate. The runs with different methanol partial pressures were also carried out at 698 K. A useful method for distinguishing the type of product and the type of deactivation is the yield-conversion plot [68]. The product yields at different space velocities versus the conversion at 698 K and a methanol partial pressure of 7.2 kPa are available in [69].

It mentions that methane is a stable primary plus secondary product [70,71,72]. A mechanism for methane formation has been proposed:



Another reaction is [15,19]:



However, both mechanisms may help to cause to the methane formation. The reaction network is given by Fig-

ure.2 that illustrates only the possible pathways for olefin formation from DME.

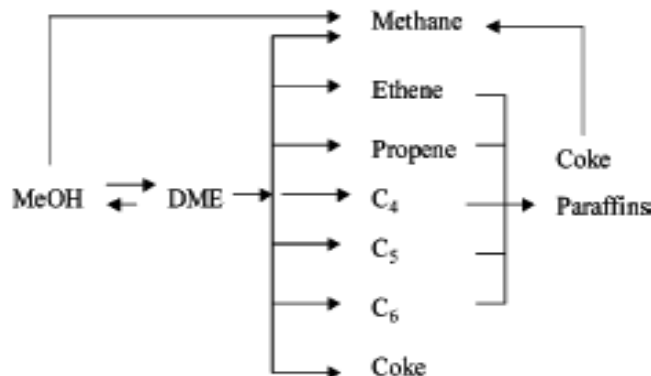


Figure. 2. Reaction network for MTO over SAPO-34. Adapted with permission from [69].

In this series of experiments, four effects that influence Selectivity during MTO on SAPO-34 were studied.

- Effect of Space Velocity. All the OPE (optimum performance envelopes [68,73]) lines are linear for the hydrocarbons, so the selectivity are independent of conversion (or space velocity).
- Effect of Partial Pressure. At constant coke content, Product selectivity was independent of the partial pressure.
- Effect of Temperature. The selectivity to ethene and methane increases when the temperature increases, whereas the selectivity of propene decreases. C<sub>4</sub> and C<sub>5</sub> selectivity are only slightly influenced.

As described previously, the coke selectivity increases significantly with temperature [74].

- Effect of Temperature. When the temperature increases, the selectivity to ethene and methane increases while the selectivity of propene decreases. C<sub>4</sub> and C<sub>5</sub> selectivity are only slightly influenced.
- Effect of Coke Deposition. The degree of deactivation due to coke deposition affected the Product selectivity and the yields of C<sub>3</sub>-C<sub>6</sub> olefins on a catalyst containing coke were lower than on the fresh catalyst at a given conversion.

While the opposite tendency was observed for ethene, it was found that selectivity of the olefins decreases with coke content as follows:

C<sub>6</sub> > C<sub>5</sub> > C<sub>4</sub>, C<sub>3</sub>

Coke deposition increases with increasing temperature as shown in the previous work [74].at the higher temperature, the conversion of oxygenates decreases with time on-stream as it is indicated in [69]. The present work shows that deactivating effect of coke molecules formed during MTO at different temperatures. So at high temperatures, the rapid coke deposition causes the rapid deactivation of oxygenates.

**Table 4.** Reaction Rate Constants,  $k_i^0$ ; Deactivation Rate Constants,  $\alpha_i$ , at Different Temperatures and Parameters for Arrhenius Equation  $k_i^0 = A_i \exp(-E_i/RT)$ . Adapted with permission from [69].

	$T, ^\circ\text{C}$				$A_i$ (kmol/g <sub>cat</sub> , kPa, h)	$E$ (kJ/mol)
	400	425	500	550		
$k_1^0$	$0.22 \pm 1 \times 10^{-2}$	$0.25 \pm 1 \times 10^{-2}$	$0.55 \pm 5 \times 10^{-2}$	$0.755 \pm 6 \times 10^{-2}$	7210	38.4
$k_2^0$	$0.35 \pm 1 \times 10^{-2}$	$0.31 \pm 1 \times 10^{-2}$	$0.67 \pm 5 \times 10^{-2}$	$0.76 \pm 6 \times 10^{-2}$	40	27.0
$k_3^0$	$0.13 \pm 1 \times 10^{-2}$	$0.11 \pm 1 \times 10^{-2}$	$0.23 \pm 5 \times 10^{-2}$	$0.28 \pm 5 \times 10^{-2}$	15	26.9
$k_4^0$	$0.038 \pm 2 \times 10^{-2}$	$0.035 \pm 2 \times 10^{-2}$	$0.087 \pm 1 \times 10^{-2}$	$0.104 \pm 2 \times 10^{-2}$	17	49.8
$k_5^0$	$0.008 \pm 9 \times 10^{-3}$	$0.011 \pm 6 \times 10^{-3}$	$0.017 \pm 1 \times 10^{-2}$	$0.030 \pm 9 \times 10^{-3}$	5	32.4
$k_6^0$	0	$0.006 \pm 5 \times 10^{-3}$	$0.020 \pm 1 \times 10^{-2}$	$0.028 \pm 9 \times 10^{-2}$	181	59.6
$\alpha_1$	$0.038 \pm 1 \times 10^{-3}$	$0.049 \pm 3 \times 10^{-4}$	$0.054 \pm 3 \times 10^{-3}$	$0.063 \pm 1 \times 10^{-3}$		
$\alpha_2$	$0.041 \pm 1 \times 10^{-3}$	$0.052 \pm 3 \times 10^{-4}$	$0.059 \pm 2 \times 10^{-3}$	$0.066 \pm 1 \times 10^{-3}$		
$\alpha_3$	$0.040 \pm 2 \times 10^{-3}$	$0.052 \pm 8 \times 10^{-4}$	$0.054 \pm 4 \times 10^{-3}$	$0.058 \pm 3 \times 10^{-3}$		
$\alpha_4$	$0.050 \pm 8 \times 10^{-3}$	$0.060 \pm 6 \times 10^{-4}$	$0.060 \pm 1 \times 10^{-2}$	$0.062 \pm 6 \times 10^{-3}$		
$\alpha_5$	$0.115 \pm 4 \times 10^{-2}$	$0.114 \pm 3 \times 10^{-2}$	$0.059 \pm 1 \times 10^{-2}$	$0.065 \pm 1 \times 10^{-2}$		
$\alpha_7$	$0.066 \pm 3 \times 10^{-2}$	$0.066 \pm 2 \times 10^{-2}$	$0.057 \pm 3 \times 10^{-2}$	$0.072 \pm 2 \times 10^{-2}$		

The conversion of oxygenates in the model of the previous work [74] was treated as a first-order reaction. The kinetic models for coke deposition and the conversion of oxygenates were developed in the present work, the integral model is used for methanol conversion and the model is investigated to foretell the selectivity change with coke formation. Also for fitting the parameters in the deactivation functions, the experimental coke contents were used. All mole fractions are calculated on a dry basis and on the basis of CH<sub>2</sub> equivalents. The reactor models are declared as follows:

$$\frac{d\bar{x}}{d(W/F_{\text{MeOH}})} = \bar{r} \quad (29)$$

The kinetic model is expressed for the reaction network in Figure 2:

$$r_i = k_i^0 \phi_i y_6 P_0 \text{ for } i=1-5 \quad (30)$$

$$r_6 = (\sum_{i=1}^5 k_i^0 \phi_i) y_6 P_0 \quad (31)$$

Where  $i =$  [ethene, propene, butenes (C4), C5, C6, oxygenates, ethane + propane]. The paraffins formation the rate of the paraffins formation is depicted as follows:

$$r_7 = k_7^0 \phi_7 (1-y_6) P_0 \quad (32)$$

where  $k_i^0$  is the initial rate constant,  $\phi_i$  is the deactivation function,  $P_0$  is the initial methanol partial pressure, and  $y_i$  is the mole fraction on a CH<sub>2</sub> basis.

All rate constants, which are considered by the deactivation functions, are supposed to depend on the catalyst coke content,  $\phi_i$ . The best fit to the experimental data is given by linear function as follows:

$$\bar{\phi} = 1 - \bar{\alpha} C \quad (33)$$

$C$  is the weight percent of coke on the catalyst ( $\text{g}_{\text{coke}}/\text{g}_{\text{cat}}$  %). The effect of coke on the selectivity is modeled by using different values for the empirical deactivation constants,  $\alpha_i$ .

For integrating the ordinary differential equations, a fourth-order Rung-Kutta method was used. The parameters of the kinetic model have been estimated by the nonlinear

least-squares routine in MATLAB using the Levenberg-Marquardt method. The optimum function is given:

$$S = \sum_{i=1}^n \sum_{j=1}^m w_{ij} [(y_{iPR}) - (y_{iEXP})] \quad (34)$$

Where index  $i$  indicates the component considered; index  $j$ , the kinetic run;  $y_{iPR}$  and  $y_{iEXP}$  are the predicted and experimental molar fraction for component  $i$ ; and  $w_{ij}$  is a weighting factor. Table 4 shows Reaction and deactivation rate constants together with their standard deviations. The overall regression is meaningful that is indicated by Statistical analysis.

An Arrhenius plot of the initial kinetic rate constants for the formation of the various products is available in [69]. The rate constants fitted Arrhenius law well. The estimated apparent activation energies and pre-exponential factors are listed in table 4.

The comparison between experimental and predicted mole fractions for each component is performed by the present work. By using the parameters listed in Table 4, the Arrhenius equation calculated the rate constants. The model had a good fit for the experimental results generally at all temperatures, except for methane and C6 because the mole fractions for C6 and methane are very low at the conditions used in the present work.

#### Nomenclature

$A_i$  = pre-exponential factor for the reaction rate,

$k_i^0$ , kmol (g of cat, kPa, h)<sup>-1</sup>

$C$  = weight percent of coke on the catalyst (g of coke/100 g of cat)

$E$  = activation energy, kJ/mol

$F_{\text{MeOH}}$  = molar flow rate of methanol (mol/h)

$i = 1, 2, 3, 4, 5, 6, 7$  represents ethene, propene, butenes (C4), C5, C6, oxygenates, and ethane + propane, respectively.

$j$  = number of kinetic run

$k_i^0$  = initial rate constant for the formation of component  $i$ , kmol (g of cat, kPa, h)<sup>-1</sup>

$P_0$ : initial methanol partial pressure, kPa

$\bar{r}$  = [ $r_1, r_2, r_3, r_4, r_5, r_6, r_7$ ]; matrix of reaction rate, kmol (g of cat, h)<sup>-1</sup>

$r_i$  = rate of formation of  $i$ , kmol (g of cat, h)<sup>-1</sup>

$S$  = objective function

W= catalyst loading, g of cat

w<sub>i</sub> = weighting factor.

$\vec{x}$  = [x<sub>1</sub>, x<sub>2</sub>, x<sub>3</sub>, x<sub>4</sub>, x<sub>5</sub>, x<sub>6</sub>, x<sub>7</sub>]; matrix of conversion

x<sub>i</sub> = conversion to i

y<sub>i</sub> = mole fraction of component i on a CH<sub>2</sub> basis

y<sub>iEXP</sub> = experimental molar fraction for component i

y<sub>iPR</sub> = predicted molar fraction for component i

α<sub>i</sub> = empirical deactivation constant for the reaction corresponding the formation of i defined by Eq.(33)

φ<sub>i</sub> = deactivation function for the formation of component i

## CONCLUSIONS

This review suggests different kinetic modeling of deactivation of SAPO-34 catalyst during Methanol to Olefins (MTO) process. The deactivation is attributed to higher oligomerization products that cover the acid active sites and/or block pores which results in decreasing the methanol conversion and the yields of the various products.

The relation between the coke content over SAPO-34 and the cumulative amount of methanol fed, amount of hydrocarbons formed per gram of catalyst, reaction time and rate is presented in this review. These models describe the effect of deactivation on olefin formation and presents deactivation functions for the methanol conversion, the yields of olefins etc. Effects of space Velocity, partial pressure, temperature on coke deposition are investigated During MTO on SAPO-34.

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