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Study of coke behaviour of catalyst during methanol-to-olefins process based on a special TGA reactor

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ABSTRACT

Thermax 700 thermo-gravimetric analysis (TGA) instrument with large weight capacity is introduced for the investigation of the coke formation of SAPO-34 catalyst during methanol-to-olefin (MTO) process in this study. By the use of a special sample basket and relatively higher methanol concentration, the TGA instrument can be viewed as fixed-bed reactor, while both coking rate and reaction results for MTO reaction can be recorded *in situ*. The influences of reaction conditions over coking rate are discussed, while the effect of temperature is emphasized. Both weight change and color interchanging phenomenon at different reaction temperatures indicate that the severity of hydrothermal atmosphere is partly responsible for the different species of coke formation as temperature varies. A simplified coking model with exponential mathematical expression is established and verified. Coking has a very close relationship with MTO results. The different trend of product distribution as coking occurs proves the selective deactivation phenomenon. DME can be viewed as an indicator of the deactivation level in this process. The coking model is valuable to express the catalyst activity change during reaction as well as kinetic modeling for further investigations, while the catalyst coke content during MTO process can be predicted simultaneously.

1. Introduction

Reaction of methanol-to-hydrocarbons was first discovered in the laboratory of Mobil Company in 1970s based on ZSM-5 catalyst [1]. It was noticed that the alternation of reaction conditions favored the olefins products [2,3], namely methanol-to-olefins (MTO) reaction. The oil crisis in 20th century accelerated this study, which was proved to be a feasible way to obtain light olefins, particularly ethylene and propylene, from non-petroleum feedstock.

The discovery of small-pore molecular sieve [4] named as SAPO-34 was proved to be the most suitable catalytic material for MTO reaction in 1984. Based on this catalyst, UOP promoted the MTO process technology in 1990s, together with Norsk Hydro Company [5]. The fundamental research of MTO mainly involves the study of catalyst preparation and reaction mechanism. The mechanism of MTO reaction in terms of SAPO-34 catalyst, especially the route for the first C–C bond formation, had long been in dispute [6]. In recent years, a parallel reaction mechanism named as Hydrocarbon Pool Mechanism advanced by Dahl et al. [7,8] has been testified by many researchers [9]. Based on this mechanism, many lumping kinetic models had been proposed as well [6,10].

The deactivation of SAPO-34 caused by coking during MTO reaction has long been studied [6]. Bos et al. [11] proposed a lumped kinetic model with consideration of coke as a lumping species firstly. However, direct measurements of coke content inside fixed-bed reactor must be conducted by methods such as burning off coke in the reactor [12] or taking off catalyst outside for weighing [11] or coke scanning [13], will bring into additional errors, and it is also a time consuming process. A tapered element oscillating microbalance (TEOM) reactor was first introduced into MTO study *in situ* by Chen et al. [14], and was proved to be a powerful tool for the study of coking. The operation of TEOM is based on the relationship between the natural frequency of the oscillating tapered element containing the catalyst and its mass. Therefore, the contact between sample basket and reaction stream can achieve 100%, and the vibration frequency of tapered element can be interpreted and translated into mass signal continuously. Based on TEOM, Chen et al. [10,15] gave a description of coking behavior and kinetic model including catalyst deactivation for SAPO-34 during MTO process. Intermediates generated by oxygenates inside the pores of SAPO-34 catalyst, was assumed to be the precursors of deposited coke, which is in accord with Hydrocarbon Pool Mechanism. The effects of properties of SAPO-34 catalyst on coking behavior were investigated [16], while the diffusion and adsorption phenomena influenced by coke deposition were studied as well [17,18].

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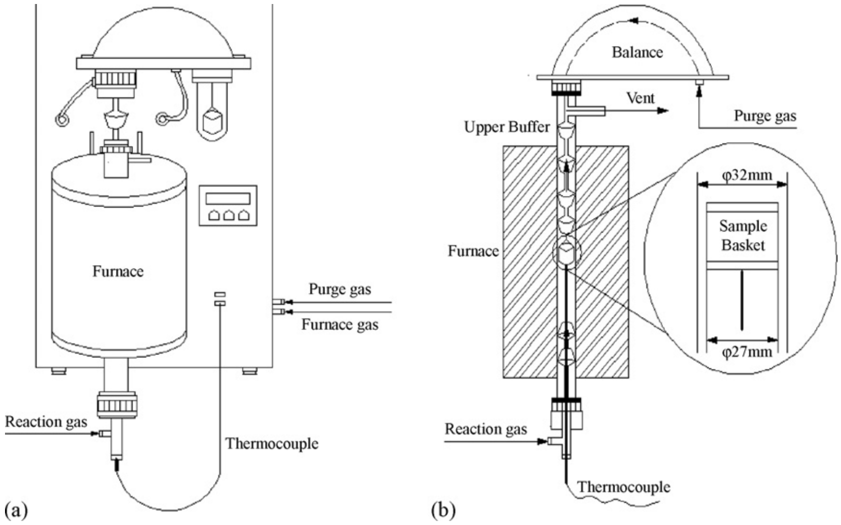

Fig. 1. Schematic of Thermax 700 TGA instrument of both external (a) and internal (b).

The behavior of coke deposition is important to the kinetic study and reactor design. Froment [19] gave several empirical formula related coke content with catalyst activity. Classical coking model was proposed by Voorhies in 1940s and was widely accepted, which described coke content as a function of reaction time (TOS). Chen et al. [15] deduced an elaborate coking model which related coking rate with reaction conditions, TOS and accumulated methanol feed in terms of oxygenates conversion. Qi et al. [13] also proposed a simplified model of coke deposition, which is regressed with cumulated methanol feed only. The method of relating coke content with feed conversion is helpful to reactor design, for the profiles of coke distribution can be obtained. However, the prediction of average coke content in catalyst bed during reaction cannot be performed without kinetic data.

Recently, the production of TEOM has been suspended by Thermo Company. It is hence necessary to find substitution methods for the study of coking behavior. Direct weighing method such as using electro balance equipment was reported by early scholars [20,21], and was proved to be a possible choice by operating in a differential mode. However, because of the typical high ratio of diameters between reaction tube and sample basket (15 mm/8 mm) [14], the “bypass” phenomenon was found to be a primary disadvantage, for any contact between sample basket and reaction tube would generate error data. Fortunately, Thermax 700 thermo-gravimetric analysis (TGA) instrument (Thermo Company, America) with high weight capacity and resolution was introduced by Thermo Company. Sample basket with larger inner diameter can be used results from its 100.0 g weight capacity, hence is helpful for the elimination of “bypass”. As a whole, Thermax 700 is a direct weighing instrument and has an obvious advantage by comparison with traditional electro balance method, because of its high weight capacity. It is also a feasible substitution of TEOM reactor, and the accumulated error in data interpretation and translation processes can be avoided, although the elimination of “bypass” phenomenon must be checked.

Bypass belongs to external diffusion problem which can be verified by using experimental methods in kinetic study [14]. The comparison of Thermax 700 TGA reactor and fixed-bed reactor as well as the verification of diffusion elimination is performed by using such methods. The weight change of catalyst during MTO process is investigated in detail, while the effects of reaction conditions especially reaction temperature on coking rate are discussed. Additional characterizations for coked catalyst are performed as well; focusing on the influence of temperature on the type of coke deposited. A simplified coking model in terms of initial reaction conditions and TOS is established to predict the average coke content of SAPO-34 in catalyst bed, which is also helpful to reactor design when combining with the empirical equations related average coke content with catalyst activity.

2. Experimental

2.1. Catalysts preparation

SAPO-34 catalysts are prepared as described previously [4]. Aluminium isopropoxide and an aqueous solution of orthophosphoric acid with 30 wt% are mixed and stirred into homogenous, while a colloidal solution of 30 wt% SiO_2 and a 40 wt% template agent of TEAOH solution are added to the resulting mixture during stirring consequently. The crystallization is carried out in a 1 L titanium autoclave under 473 K and the auto generated pressure for 99 h, with a stirring speed of 200 rpm. The catalyst is separated from the liquid phase by centrifugation and water washing after cooling. The organic template is eliminated by calcination in a muffle furnace at 823 K for 4 h, while the calcinated catalyst is conserved in ambient environment. The catalysts are smashed and sieved into a uniform distribution of crystal size with 125–154 μm for experimental use.

The crystallinity and integrity of the zeolite materials are further verified by X-ray powder diffraction, and are proved to be pure SAPO-34 molecular sieve. Surface area with 506.99 m^2/g and 0.32 cm^3/g pore volume is detected by BET method from isotherm data of nitrogen adsorption–desorption obtained at 77 K using ASAP 2020 analyzer (Micromeritics, America). Total acid strength of 1.12 mmol/g by TPD method are obtained by temperature programmed desorption (TPD) of NH_3 from 373 to 973 K in a heating rate of 10 K/min by AutoChem 2920 analyzer (Micromeritics, America).

2.2. Introduction of TGA reactor

The core instrument in the experimental system is Thermax 700 TGA instrument, as shown in Fig. 1. It is a special TGA instrument with both large weight capacities (100.0 g) and balance resolution (1 μg). Therefore, special sample basket with large diameter can be adopted, which would help to eliminate the “bypass” phenomenon. The reaction gas of methanol with nitrogen effluent is forced to pass through the catalyst bed from the bottom of the furnace tube, while

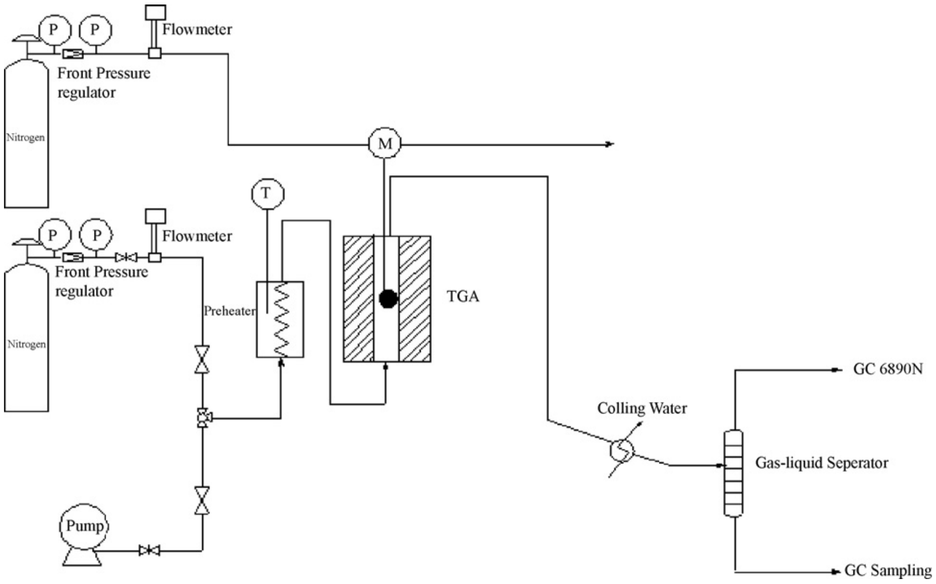

Fig. 2. Flow scheme of catalyst test experiment for MTO process.

the reacted stream is released from the outlet at the top of furnace tube.

SAPO-34 catalyst is loaded inside the bronze sample basket, so that any slight change of catalyst weight can be recorded *in situ*, with a 0.5 s recording frequency. The sample basket is specially made with screen bottom of 71 μm pore diameter and 27 mm external diameter, and is placed in the isothermal region inside the reaction tube. The reaction tube is 460 mm in length with 32 mm inner diameter, and is highly sustainable even at 1973 K temperature and a 120 K/min heating rate. The value of 32/27 for Thermax 700 is much bigger than that for common electrobalance [14], which is crucial to the elimination of "bypass" phenomenon in relatively lower methanol concentration. Besides, the existence of upper buffer designed at the top of the sample basket is also helpful to increase the contact ratio between feed and catalyst, because reaction streams are forced to flow through the hollow channel of the upper buffer. It has been checked that the catalyst powder keeps stationary under the flow of reaction stream. A stream of purge gas is introduced into the TGA system for the avoidance of the direct contact of reaction gas and electrobalance equipment. However, there is no mixing phenomenon for the 2 streams, because the flow rate of purge gas is constantly lower.

Based on this TGA instrument, MTO reactions are performed under relatively larger space velocities with consideration of "bypass" elimination. Analytical grade of methanol feed with a concentration of 99.5% (wt%) is introduced into the reaction system in every reaction condition. Different methanol partial pressures ranging from 8.53 to 28.50 kPa are utilized to study the weight change of SAPO-34 under atmospheric pressure by nitrogen addition. Influence of reaction temperature is also investigated, with a range from 648.2 to 773.2 K.

2.3. Catalyst test

The schematic diagram of catalyst test is illustrated in Fig. 2. Methanol feed is injected into reaction system from the constant flux pump, with nitrogen as diluent. The preheated effluent is introduced into TGA reactor from its inlet, and start MTO reaction inside the reaction tube. Milligrams of SAPO-34 molecular sieves are loaded at the bottom of the bronze sample basket, while the feed gas can contact with the catalyst through the sieve pore in an intermediate way. The reaction products and unconverted feed are separated into 2 phases by a gas–liquid separator after cooling under circulated water outside TGA reactor, and analysed by GC 6890N and 6820 (Agilent) equipped with capillary HP PLOT-Al_2O_3/KCl and PLOT-Q columns, by using pressure and temperature programming methods as well as an FID and TCD detector respectively. The velocity of tail gas is calculated by a soap film flow meter, which is used for the verification of total mass balance.

Because of the high selectivity for olefin products of SAPO-34 catalyst, total amount of hydrocarbon products including dimethyl ether (DME) is released from gas phase, while generated water and unconverted methanol can be collected from liquid phase. Trace amount of DME can be detected as well. The material balance relationship for all the compounds is carefully checked based on a material and carbon balance including coke formation. The material balance error is limited in the range of ±1.5% in each test.

3. Results and discussion

3.1. Weight change of SAPO-34 catalyst during MTO process

Blank experiment with no catalyst loading under a methanol flow rate of 0.04 ml/min proved that the weight change of sample basket is negligible, which is demonstrated in Fig. 3. Because of the dedicate design of furnace system in the Thermax 700 TGA instrument, the temperature variation can be controlled in a range of ±0.3 K even after the injection of methanol feed. Therefore, the gradient of temperature distribution in the sample basket can be assumed to be insignificant under a 200 mg catalyst loading.

The dehydration of SAPO-34 during heating process has been observed by TGA instrument. The DTG curve obtained in Thermax 700 TGA indicates a sharp dehydration peak between 373 and 473 K for calcinated SAPO-34 catalyst preserved in ambient atmosphere. The dehydration amount is roughly 22% (wt%) in every circumstance, which is indicated as Fig. 4. Therefore, the space velocity is not the real value if defined on the basis of hydrous catalyst. Dehydrated weight is used for the calculation of WHSV in this study.

The weight increase of SAPO-34 catalyst is soon detected after methanol injection. Chemical adsorption phenomenon is reported as a reason accounts for the weight increase as well as coking [18]. Nitrogen stripping is used to distinguish the ratio of coke and adsorbates during reaction process, which is illustrated in Fig. 5a. The adsorbates can be stripped off from the catalyst surface by flow

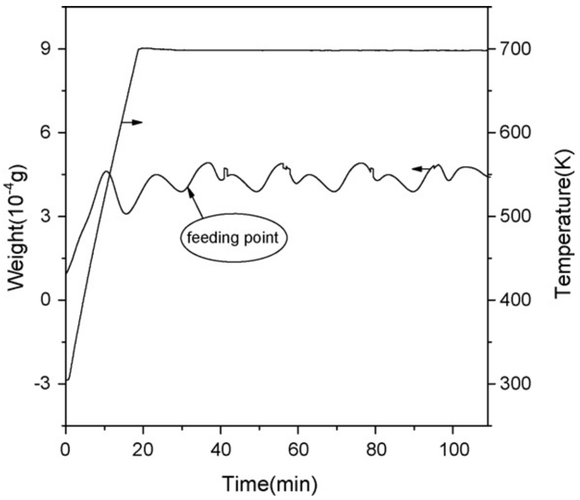

Fig. 3. Weight change of sample basket without catalyst loading.

stream, while real coke formed remains constant. However, the amount of adsorbates is relatively small compared to real coke content even under severe catalyst deactivation. As a whole, ignore adsorbates would not result in an obvious error for the calculation of coke deposition.

Simultaneous thermo-analysis in Thermax 700 under 698 K for SAPO-34 during MTO reaction indicates that the coking rate is higher initially, while DTA curve also shows that the reaction heat is higher in the early stage, as depicted in Fig. 5b. TGA and DTA curves suggest that the reaction heat and coking rate slow down as reaction goes on. The weight increasing rate slows down apparently after 18% coke is deposited, while TGA curve turns into flat as weight increases by roughly 26% that can be viewed as final coke content, which is independent of reaction conditions discovered in this study. The existence of final coke content is also found by Chen et al. [15], but was not mentioned by Qi et al. [13]. However, this value is a little higher than Chen et al. (20%) [15]. The catalyst with relatively larger pore volume in this study than Chen [18] used (0.26 cm^3/g) could be the reason responsible for such difference. Meanwhile, the constant and lower reaction heat in this stage revealed by DTA curve also indicates the complete deactivation has taken place.

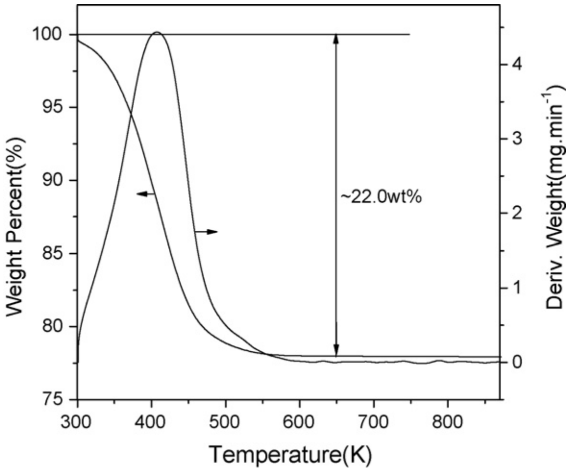

Fig. 4. TGA–DTG curves of the calcinated SAPO-34 sample in nitrogen atmosphere.

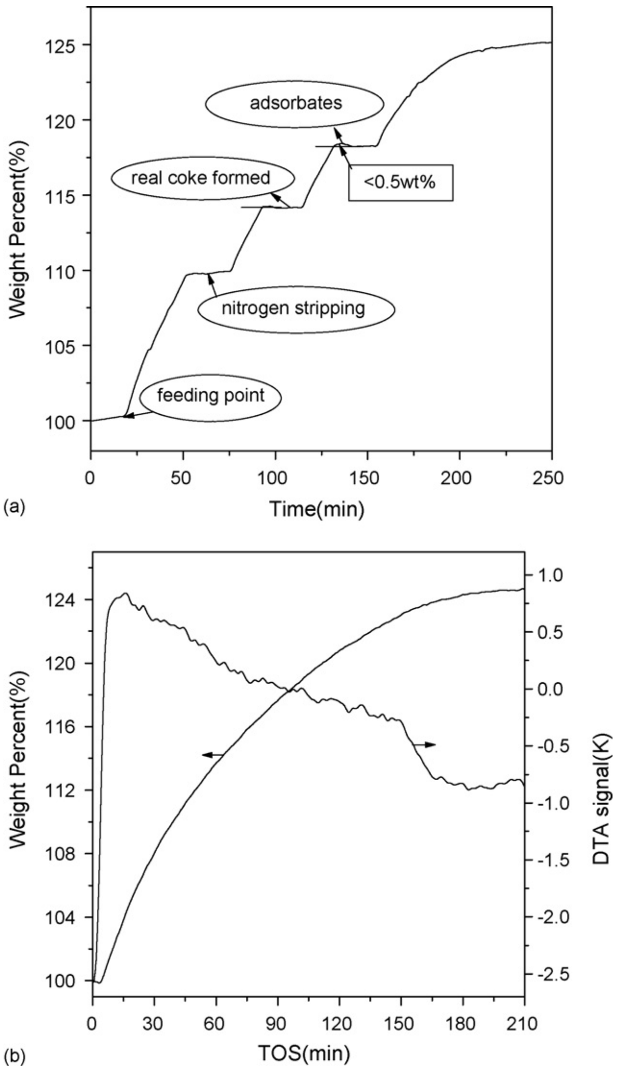

Fig. 5. Weight change of SAPO-34 with nitrogen stripping (a) and TGA–DTA curve (b) during MTO reaction.

3.2. Check of the elimination of bypass phenomenon

The annular space of 2.5 mm existing between reaction tube and sample basket will lead to a bypass of reaction stream. Although with intricate design of reaction tube and sample basket, the bed diffusion caused by “bypass” is believed to be existed in this TGA system. The coking data obtained in TGA reactor cannot be applicable if the reaction results are dissimilar with that in fixed-bed reactor. However, the mass gradient would become negligible if higher methanol concentration is adopted, according to Fick’s law. It has been tested that a lower methanol concentration of 5.06 h^{-1} (WHSV) and 8.53 kPa methanol partial pressure would lead to a decrease of methanol conversion and coking rate of SAPO-34 in TGA reactor compared to fixed-bed reactor. Therefore, a relatively higher value with 7.08 h^{-1} with 8.53 kPa methanol partial pressure is utilized for the comparison under 698 K reaction temperature and 140 mg catalyst loadings, as shown in Fig. 6a.

It is apparent that the selectivity of ethylene and propylene as well as methanol conversion are almost identical during MTO process in both reactors, which suggests that Thermax 700 TGA reactor is equal to fixed-bed reactor under such reaction conditions. The essentially coincident TGA curves for different catalyst loadings under identical space velocity of 7.08 h^{-1} is also a sign of the elimination of external mass diffusion, as presented in Fig. 6b. Since

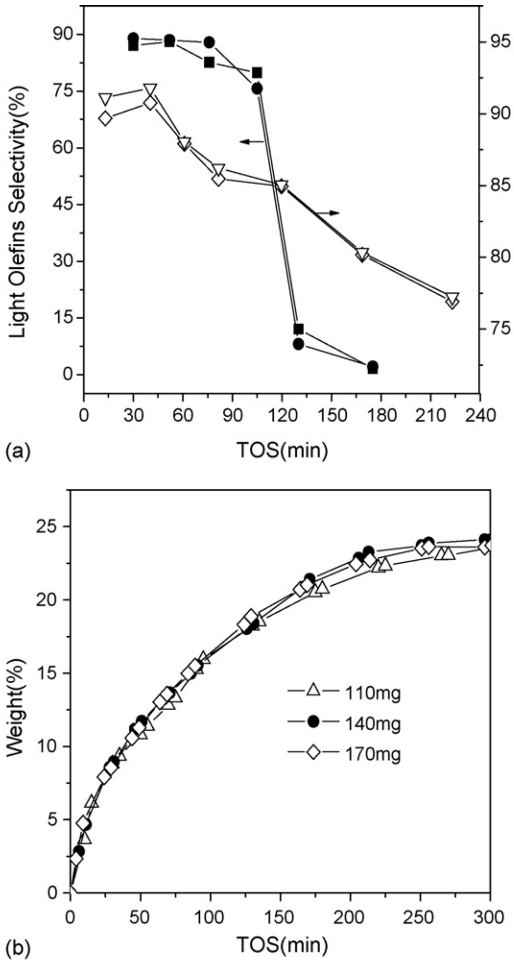

Fig. 6. Test of the elimination of bed diffusion. (a) MTO over SAPO-34 in different reactors: fixed-bed (■▽), TGA reactor (●◇); (b) weight change of SAPO-34 in TGA reactor with different catalyst loadings.

higher methanol concentration is believed to be more effective for the elimination of external mass diffusion, the conditions of the experiments performed in this study are chosen between 7.08 and 35.91 h^{-1} (WHSV) based on the dehydrated SAPO-34 weight, with methanol partial pressure higher than 8.53 kPa.

3.3. Coking model formulation

Although with a small amount of catalyst loadings and higher space velocity, the high conversion of methanol in Fig. 6a also suggests the reactor should be treated as integral plug-flow reactor instead of differential reactor. The coke distribution along the catalyst bed is expected. Therefore, it is reasonable that the coke content obtained in TGA *in situ* is the average data. According to Fig. 5b, this value has little relationship with catalyst loadings. Froment [19] had given several descriptions of the relationship between catalyst activity and average coke content. Besides, the coke content for SAPO-34 in fluidized reactor of commercial scale in MTO process is always used as the average value [22]. Therefore, the introduction of average coke content expressed as a function of reaction condition and reaction time would be a simplified substitution of coke distribution profile that can be used in reactor design as well.

From TGA curves in Fig. 6b, the curvilinear relationship between coke content and reaction time (TOS) is observed. Voorhies related coke content with TOS only, while the power function model was adopted. However, based on the coke data acquired in Thermax 700 TGA instrument, it is found that the exponential model gives a best description between coke content and TOS under a fixed reaction condition, as shown in Fig. 7. Therefore, the average coke content can be expressed as Eq. (1), while all the unknown parameters (a, b and d) are believed to have relationships with initial reaction conditions only. By the use of such coking model, information of conversion distribution data along the catalyst bed can be avoided, which makes the prediction of coke content under initial reaction conditions applicable.

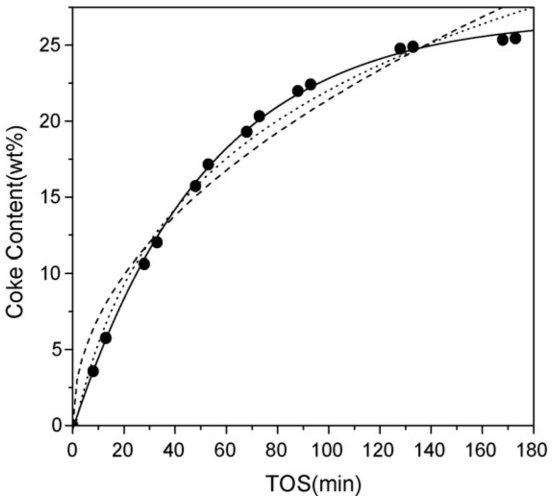

Fig. 7. The prediction of coke content by different mathematical models. (Temperature = 698.2 K, WHSV = 22.55 h^{-1}, p_{MeOH} = 12.89 kPa. —: exponential model; . . .: logarithmic model; —: power function model).

$$C = a + b \cdot e^{d \cdot t} \tag{1}$$

3.4. Effect of reaction conditions on coke formation of SAPO-34 during MTO process

3.4.1. Effect of methanol concentration

Both increasing WHSV and methanol partial pressure will lead to a variation of methanol concentration. Early scholars [13,15] proved that the coking rate accelerates as methanol concentration increases. In this study, identical results are obtained by TGA reactor, as depicted in Figs. 8 and 9.

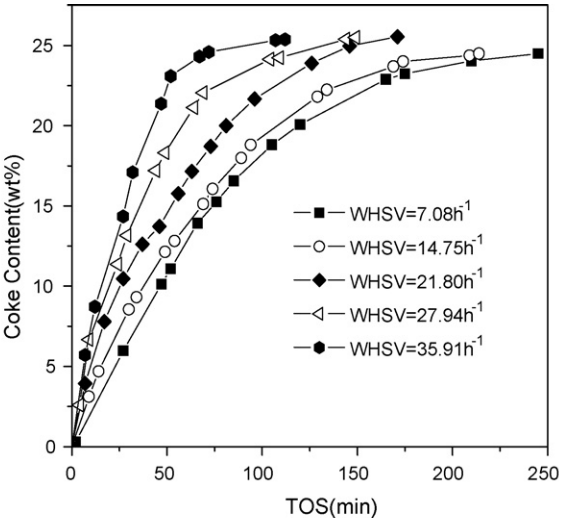

Fig. 8. Effect of WHSV on coke formation for SAPO-34 catalyst during MTO reaction (temperature = 698.2 K, p_{MeOH} = 18.50 kPa).

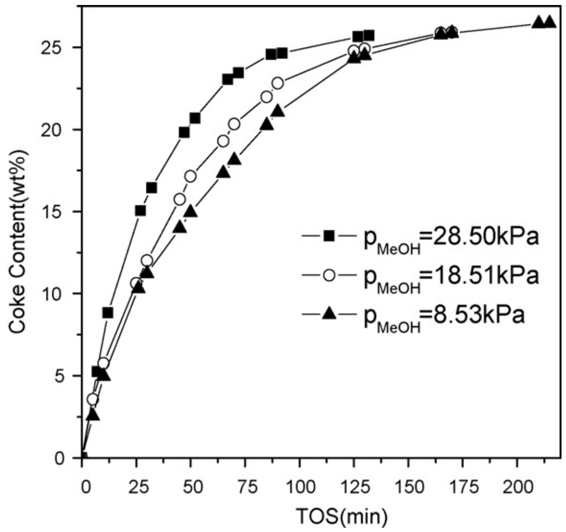

Fig. 9. Effect of methanol partial pressure on coke formation for SAPO-34 during MTO reaction (temperature = 698.2 K, WHSV = 21.80 h^{-1}).

3.4.2. Effect of reaction temperature

The influence of reaction temperature on coking rate is found to be complex. Chen et al. [15], Qi et al. [13] suggested that the coking rate is higher as reaction temperature rises, while Marchi and Froment [21] predicted that the lower temperature favors coking rate. However, it is found that higher temperature accelerates the coking rate more apparently in this study, while lower temperature also favors coke formation to a small extent, as suggested in Fig. 10.

Marchi and Froment [23] concluded that the concentration of adsorbed oligomers on the strong acid sites assumed as coke precursor may be expected to increase as temperature decreases, hence increases the coking rate. However, higher temperature will also result in the acceleration of reaction rate for higher olefins, which is also supposed to be coke precursor in higher temperatures [15]. Both higher and lower temperatures accelerate the coking rate in this study supports the two conclusions, and higher temperature is revealed to have greater impact on the coke formation. In fact, such phenomenon has also been mentioned by Guisnet et al. [24] recently. They gave a suggestion that such complex behavior can be related to the fact that the coking rate depends on the rates of chemical steps as well as retention of the coke molecules, while both the types of chemical steps and the cause of trapping depend on temperature.

It is found that the coke formed at different temperatures also produces different colors, while the color of thoroughly coked SAPO-34 catalysts varies from light yellow to dark green as reaction temperature rises from 648.2 to 773.2 K. This gives a direct suggestion that the cokes formed at different reaction temperatures are different in species. This is also in accord with the conclusions given by Qi et al. and Guinet et al. [13,24], who raised the view that the coke formed at higher temperature has a tighter structure.

By the use of Thermax 700 TGA reactor, the coke interchanging phenomena between different reaction temperatures are detected. The completely coked SAPO-34 catalyst at lower temperature will experience a period of weight decreasing while promoting the reaction temperature at hydrothermal atmosphere generated in MTO process without methanol feeding. The catalyst weight will decrease as well as the color of coked sample alters. The activity for MTO reaction of the weight decreased sample is partly recovered, and the sample will be re-coked after fed at higher temperature afterwards, which gives a proof that the temperature rising process changes the structure of the coke deposited at lower reaction temperature. Such weight changing process can be illustrated as Fig. 11a. However, this phenomenon could not be discovered as reaction temperature lowers down, as presented in Fig. 11b. The water gas reaction is assumed to take place during temperature increase and changes the formation type of coke, which gives a suggestion that coking is not only affected by the species of coke precursors but also the severity of hydrothermal atmosphere.

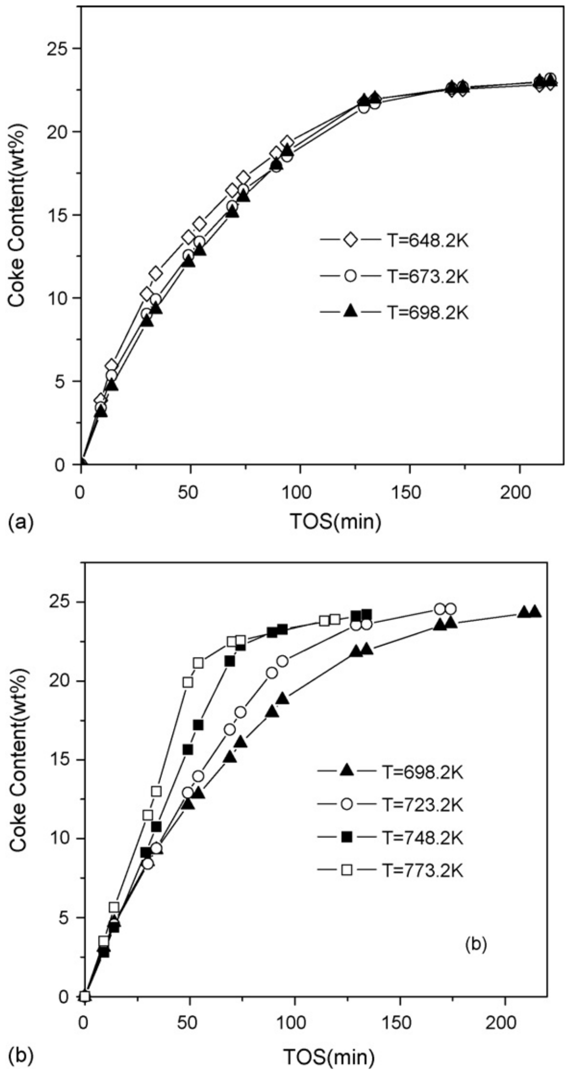

Fig. 10. Effect of temperature on coke formation for SAPO-34. (a) Lower region; (b) higher region.

3.5. Model calculation and validation

Either higher WHSV or methanol partial pressure favors the coking rate, as depicted in Figs. 8 and 9. However, the different trend of the effect of reaction temperature on coke deposition presented in Fig. 10 suggests this factor should be handled separately in coking model. According to Eq. (1), exponential function is adopted for the description of the effect of reaction temperature on coke content, while all the parameters of reaction conditions and reaction process (t) are regressed by exponential model, as given in Eq. (2).

$$C = C_0(1 - e^{\{[a+b(T/1000)+c(T/1000)^2+d(T/1000)^3]+f\cdot p\cdot WHSV\}t}) \qquad (2)$$

The estimation of the parameters of the coking model has been carried out by the nonlinear least-squares routine of Levenberg–Marquardt method using MATLAB. The optimum func-

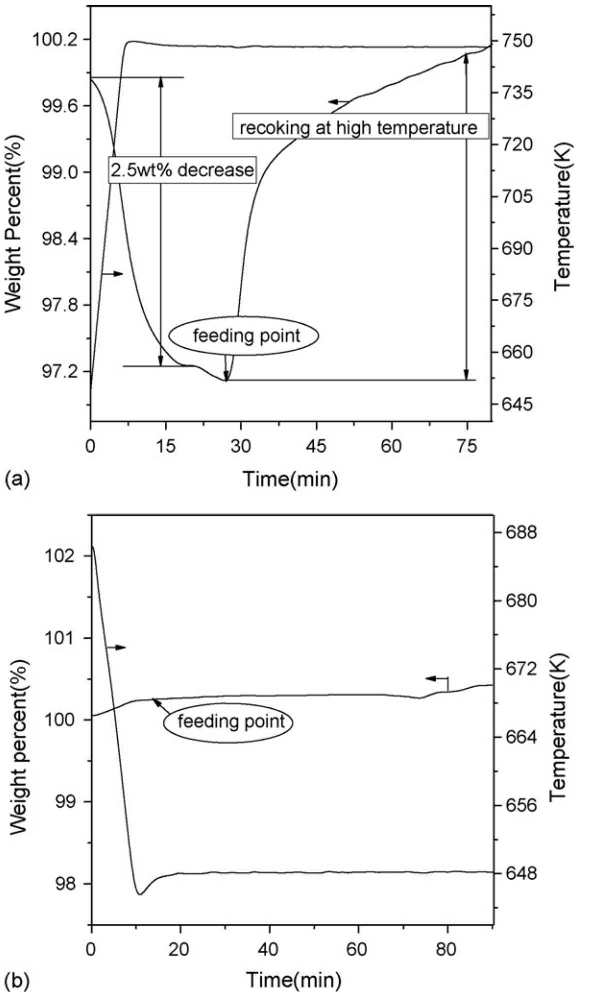

Fig. 11. Weight changes of deactivated SAPO-34 catalysts as changing reaction temperatures.

tion is described in Eq. (3).

$$S = \sum_{i=1}^{n} (C_{i,\mathrm{exp}} - C_{i,\mathrm{cal}})^2 \qquad (3)$$

where $C_{\mathrm{i,exp}}$ and $C_{\mathrm{i,cal}}$ are the predicted and experimental coke content for i^{th} experimental data with the considerations of both reaction conditions and reaction time.

All the parameters are estimated with a correlation coefficient $\rho^2 = 0.9961$, as listed in Table 1. According to Eq. (2), the parameter C_0 can be viewed as the maximum coke content can be achieved during MTO reaction for SAPO-34 catalyst, as revealed in experiments. The coke contents can be related with TOS only, under a typical initial reaction condition. Coking rate r_c can be expressed as a derivative equation of coke content, as listed in Eq. (4).

$$r_c = \frac{dC}{dt} = -C_0 A e^{At} \qquad (4)$$

where $A = a + b(T/1000) + c(T/1000)^2 + d(T/1000)^3 + f \cdot p \cdot WHSV$.

$$r_c' = \frac{dr_c}{dt} = -C_0 A^2 e^{At} < 0 \qquad (5)$$

The values of $-C_0$ and A are less than 0 under the selected reaction conditions. Therefore, as shown in Eq. (5), it can be deduced from the model that the coking rate decreases as MTO reaction goes on, which is in good agreement with the experimental data acquired from TGA reactor. The average coke content of SAPO-34 during MTO reaction is related with the initial conditions and reaction time only. All the reaction conditions are assumed to be the factors that have effects on parameter 'A'only, which is an effective simplification of the coking model.

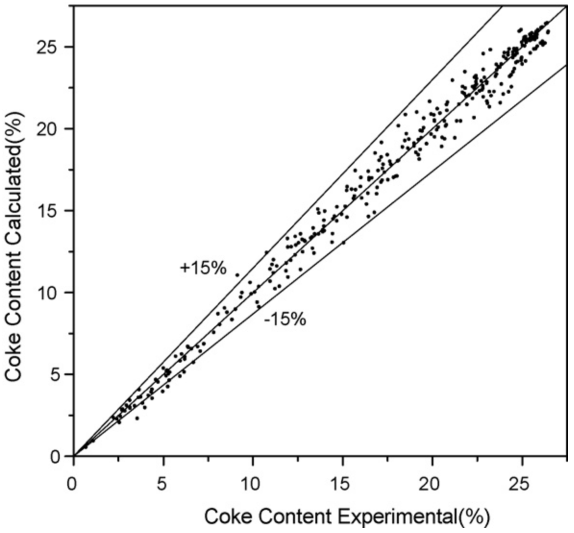

Fig. 12. Calculated versus experimental values of the coke content.

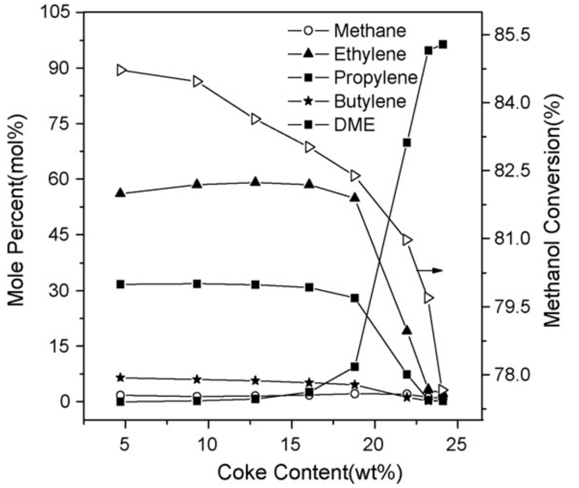

Fig. 13. Influence of coking on MTO reaction (temperature = 698.2 K, WHSV = 21.80 h^{-1}).

An extensive statistical analysis is performed. The significance of the overall regression is tested by means of an *F*-test, and the value of 986.18 is much larger than 2.60, the critical value for *F*-test under a 95% confidence level. The calculated values of coke content are presented comparatively with the experimental ones in Fig. 12. The uniformly distributed points of 355 groups of experimental data with absolute relative error no larger than 20% in this diagram also give a proof that the model selection and data regression are meaningful.

3.6. *Influence of coking on MTO reaction*

Coke deposition is the chief reason accounts for deactivation of zeolite catalyst. Based on Thermax 700, the relationship between products distribution as well as methanol conversion and the determined coke content can be depicted in Fig. 13.

Table 1
Estimated values of parameters in coking model.

	Parameters					
	C_0 (wt%)	a (min^{-1})	b (K^{-1} min^{-1})	c (K^{-2} min^{-1})	d (K^{-3} min^{-1})	f (kPa^{-1} min^{-1} h)
Values	26.78	2.27	−10.70	16.66	−8.60	−0.041

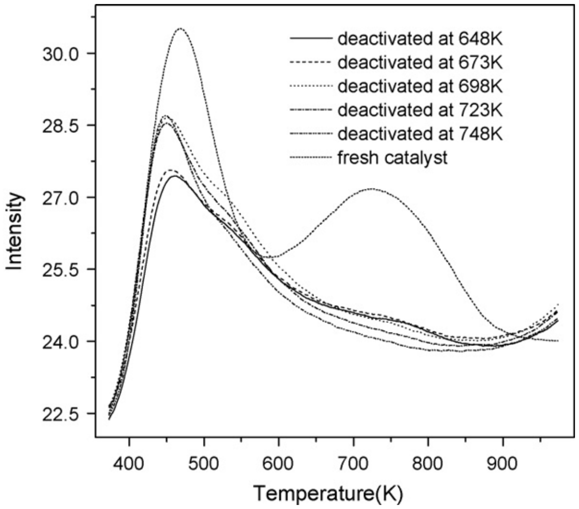

Fig. 14. TPD curves for totally deactivated and fresh SAPO-34 catalysts.

A continuously decrease of methanol conversion reflects catalyst deactivation occurs after reaction initiates. However, the distribution of MTO products varies differently as indicated by Fig. 13. The mole ratio of propylene and butylene in gas phase experiences both a mild decrease and fast decrease stages, while the trends of ethylene and methane are in a dissimilar way. Actually, the selectivity of each hydrocarbon compound changes regularly in terms of an oxygenate basis (DME is back calculated into methanol feed). Although oxygenate conversion varies with coking continuously, the selectivity for methane and ethylene increases in the whole time during reaction, while the opposite trend for propylene and butylene is detected. This is in accord with the selective deactivation explanation from Chen et al. [25].

Moreover, it can be seen that the selectivity of light alkenes changes mildly as coke content is lower than 17% or so, while ethylene yield reaches maximum at about 11% coke content. DME breakthrough appears after 18% coke is deposited, which is found to be independent of reaction condition used in this study. Methanol conversion as well as alkene yields decreases sharply as DME reaches over 5% (mol%) in gas phase, and it gives a suggestion that a higher DME amount in gas phase with the limit of reaction conditions used in this study reflects a happening of severe catalyst deactivation. From an essential view, MTO reaction can be viewed as the combination of two consecutive steps, namely methanol-to-DME (MTD) and DME-to-olefins (DTO) process [25]. Both DTO process and coking reaction are assumed to occur on the strong acid sites of SAPO-34 catalysts primarily, while MTD reaction can initiate at very weak acid sites [16]. TPD result in Fig. 14 also shows that the strong acid sites have been totally eliminated after coke content reaches the maximum value, leaving only weak acid sites. Small amount of coke deposition will result in a sharp loss of catalyst activity after 18% coke is deposited on SAPO-34 catalyst. Such phenomenon reveals that the catalyst surface has been largely covered by coke deposition, and additional coke generation would lead to a different deactivation mechanism, as reported by Chen et al. [18].

Both coke formation and initial reaction conditions have close relationships with MTO results. In this study, either lower or higher temperature is found to result in deactivation acceleration, which is in accord with the coking behavior of SAPO-34 revealed by TGA reactor. Froment et al. [19] had given several empirical correlation expressions between catalyst activity and average coke content, and can be adopted to model the deactivation kinetics for such a fast deactivation process affected by coking. The kinetic model can be acquired by the use of Thermax 700 TGA reactor. The establishment and deduction of reaction and deactivation kinetic model is of significance and complexity, which is beyond the scope of current investigations.

4. Conclusions

Thermax 700 TGA reactor is first utilized for the investigation of the coking behavior for SAPO-34 catalyst during MTO process *in situ*. The existence of “bypass” phenomenon inside reactor tube can be eliminated by adopting special sample basket and higher methanol concentration. In this case, the TGA reactor is equal to a fixed-bed reactor. The weight increase of catalyst after methanol injection includes both adsorbates and real coke, while the amount of adsorbate can be neglected.

The effects of MTO reaction conditions on the coking rate of SAPO-34 catalyst are discussed. The coking rate accelerates as methanol concentration increases. The influence of temperature on coke deposition is emphasized, while weight change and color interchanging phenomenon at different temperatures for coked samples suggest that the coke generation is not only affected by the species of coke precursors but also the severity of hydrothermal atmosphere.

It is found that the exponential model gives a best description between coke content and reaction time under fixed reaction condition. Based on the coking model established in this study, the coke content of SAPO-34 during MTO reaction is related with initial reaction conditions and reaction time, so that it can be applied in coke content prediction and reactor design conveniently. Extensive statistical tests and model analysis give a proof that the coking model is meaningful.

Coking has a great effect on MTO results, including both product distribution and methanol conversion. The selective deactivation phenomenon can be recorded as coking proceeds, while a greater change of catalyst activity can be found only after nearly 18 wt% coke is deposited on catalyst. The mole ratio of DME in gas phase can be viewed as an indicator of the extent of catalyst deactivation. Either higher or lower temperature accelerates the catalyst deactivation, in accordance with the coking behavior of the catalyst. Reaction and deactivation kinetic modeling can also be obtained based on the coke content and kinetic data in terms of Thermax 700 TGA reactor, which is meaningful for the industrialization of MTO process.

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