

# Advances in the study of coke formation over zeolite catalysts in the methanol-to-hydrocarbon process

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**Abstract** Methanol-to-hydrocarbon (MTH) process over acidic zeolite catalysts has been widely utilised to yield many types of hydrocarbons, some of which are eventually converted into the highly dehydrogenated (graphitized) carbonaceous species (cokes). The coking process can be divided into two parallel pathways based on the accepted hydrocarbon pool theory. From extensive investigations, it is reasonable to conclude that inner zeolite cavity/channel reactions at acidic sites generate cokes. However, coke formation and accumulation over the zeolite external surfaces play a major role in reaction deactivation as they contribute a great portion to the total coke amount. Herein we have reviewed previous literatures and included some recent works from KOPRC in understanding the nature and mechanism of coke formation, particularly during an H-ZSM-5 catalysed MTH reaction. We specially conclude that rapid aromatics formation at the zeolite crystalite edges is the main reason for later stage coke accumulation on the zeolite external surfaces. Accordingly, the catalyst deactivation is in a great certain to arise at those edge areas

due to having the earliest contact with the incoming methanol reactant. The final coke structure is therefore built up with layers of poly-aromatics, as the potential  $sp^2$  carbons leading to pre-graphite structure. We have proposed a coke formation model particularly for the acidic catalyst, which we believe will be of assistance in understanding—and hence minimising—the coke formation mechanisms.

**Keywords** Zeolite catalyst · Methanol to hydrocarbons · Coking · Catalyst deactivation

## Introduction

Unavoidable, progressive and intrusive hydrogen-depleted carbonaceous depositions (coke formation) have long been recognised as the most prevailing reason for practical zeolite catalyst deactivation leading to significant problems of great technical, economic, and environmental concerns [1]. Bulky coke contents, once formed within and spread over the zeolite porous system, invariably lead to a reduction in the number of catalytically active sites, and often a dramatic concomitant decrease in zeolite cavity volume and available surface area. As a result, the reaction process is interrupted with the mass transportation of reactant and product generation undesirably blocked [2–8].

Methanol has been recognised as one of the most important and versatile platform products in the energy and fine-chemical industries [9]. It is primarily used to produce a wide range of high-value chemicals, such as olefins, aromatics as well as gasoline, or their derivations as important component of green-fuels (e.g., bio-diesel) [10, 11]. The potential benefits rely on a wide choice of methanol sources from different carbon-based materials,

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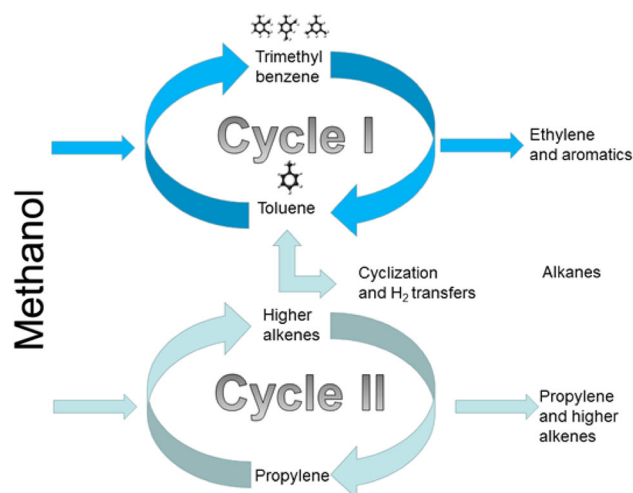
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even the biomass. For instance, it has been shown that the catalytic conversion of methanol to hydrocarbon is a highly promising route for converting natural gas and coal, even plant wastes to petrochemicals and fuels [9, 12]. This process always employs acidic zeolite catalysts on which coke formation now represents arguably the major concern for reaction deactivation. There have been many explorations and related studies dived into the process of zeolite deactivation by catalytic coke formation; however, the detailed coking mechanism, especially for specifying the differential contributions by the zeolite internal and external surfaces, respectively, is still being completed with those new findings in more recent works [1, 12–14]. In this combined review, we will address the recent progresses on the study of coke formation at different zeolite positions, particularly for the case of an acidic ZSM-5 catalyst system employed in the methanol to hydrocarbon process [15–19].

### Coke formation: a brief overview of models and mechanisms

Generally, coke evolution must be a dehydrogenation process in which hydrogen is continuously extracted from the deposited and depositing products that cannot then be moved continuously from the system [1–4]. However, the exact coke formation process appears to vary across different reaction types. For methanol-to-hydrocarbon reactions, the underlying mechanism appears to be even more complex than any other normal chemical dehydrogenations [20–22], which is within the recently developed dual-pathway theory: the initial poly-methyl aromatics/alkenes based catalytic centres (hydrocarbon pools that catalyse the reaction through multiple steps of non-stopping alkylation/de-alkylation) derive from organic impurities in the feed-stock [23], then rapidly breed and continuously split off light olefins; on the other hand, through series of product intra-conversions (hydrogen transfers) driven by thermo-conditions, more aromatics and olefinic/aliphatic species are produced, all of which are finally converted into condensed poly-aromatics, and eventually, into graphitic carbonaceous species [1, 12, 13, 24]. The dual-pathway mechanism of methanol-to-hydrocarbons is illustrated schematically in Fig. 1 [25].

From the perspective of different positions in a zeolite structure, it has been generally accepted that coke-resulted zeolite deactivation proceeds in a parallel way both inside the zeolite pores and channels, on the other hand, over the outside surfaces, which can be described by two different modes, respectively, [26]. In most cases, the geometry of reaction products is greatly limited by the zeolite porous/channel space, inside which most of the methylene-chloride-soluble (MCS) lower molecular weight coke species



**Fig. 1** Represented and adjusted dual-pathway reaction route for MTH reactions from Bjørgen et al. [14]

(smaller, less condensed carbonaceous compounds dissolved in MCS) are initially accumulated during the earlier reaction period [26, 27]. Those are simple, mainly single-aromatic-ring based species, in which a large proportion are retained inside the zeolite pores until the end of the reaction and often display a ‘primary-graphite’ status. Unsuccessful expansion of molecular structure is the typical feature of these initial coke precursors [1], e.g., a poly-methyl benzene molecule fails to expand its aromatic ring structure and hence is trapped inside the zeolite channel in a H-ZSM-5 catalysed MTH reaction. Notably, those MCS, smaller and less-dehydrogenated aromatics also perform as the catalytic centres in the methanol conversions (important hydrocarbon pool molecules, as a ‘scaffold’ for C-H bond assemblies) [12, 21, 25, 28, 29], where strong evidences for their existence and catalytic functions have been achieved by dissolving the zeolite framework to liberate the inner cokes species [1, 21, 26, 28–30].

Of course, the larger surface area of the zeolite catalyst enables both expanded and more condensed coke species to be formed and gradually build up, which also leads to the deactivation of zeolite catalyst by blocking the pore/channel openings from the outside and this clearly inhibits any mass transportations accompanying the reaction. External coke species, as a result of further aromatization and hydrogen deficiency [29, 31, 32], are mainly deeply graphitized poly-aromatics showing poor solubility in methylene chloride (methylene chloride insoluble, MCI) [26, 30]. They are typically visually seen in the form of either small concentrations of black carbon particles or an envelope shape around the zeolite crystals which remains as an empty mould after zeolite solubilisation [1, 26, 30].

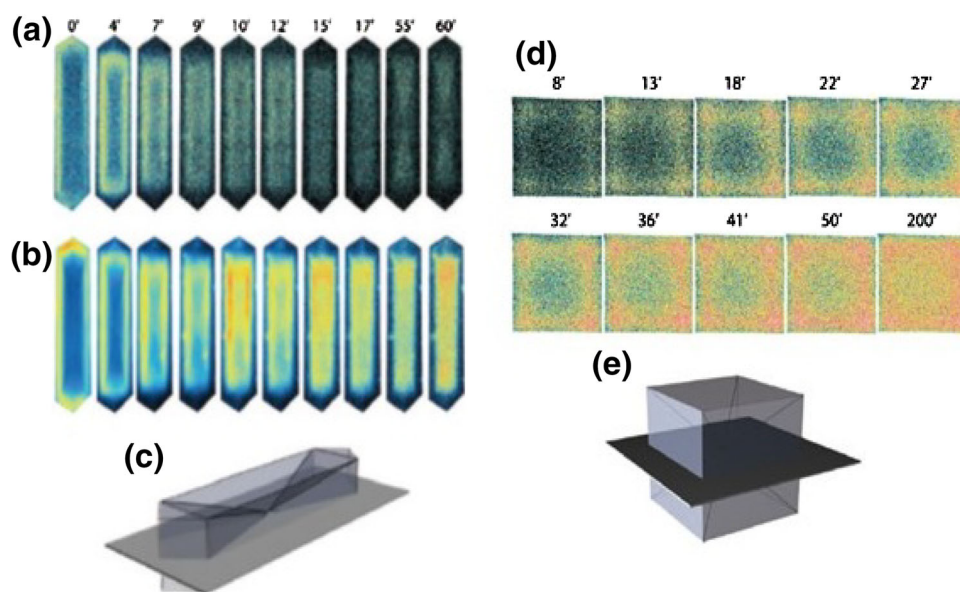
### Coke accumulation originates at regions near zeolite edges

Given the fact that a large portion of zeolite Brønsted acid sites are located inside the zeolite pores/channels [33], it seems that the first sign of possible coke/precursor accumulation often emerges at the zeolite crystal edges, which is observable even at the initial period of reaction. In the work of Mores et al. [14], confocal fluorescence microscope was employed in an upright configuration to capture the formation of coke species and their precursors inside the zeolite grains. It was noted that fluorescence-marked methyl benzenes (major coke precursors) were firstly built up at the zeolite crystal edges, and this was the case for both H-ZSM-5 and H-SAPO-34 catalyzed reactions (Fig. 2). The captured fluorescence patterns show that the accumulation of methyl benzenes gradually moved inwards to the cores of the zeolite crystal. However, for H-ZSM-5 catalyst, the inner migration of coke species halted much earlier, whereas for H-SAPO-34 there was a gradually progressing process, and by the end of reaction the inner pores of H-SAPO-34 were totally filled with methyl benzenes [14].

One most possible explanation for the coke accumulation starting at the zeolite crystal edges would be a priority to have a first contact with the reactant feedstock for those zeolite edge regions, much earlier than the inner cavity/

channel areas. Therefore, it is reasonable to imagine a faster product/coke precursor building up first at those sites near zeolite edges, and particularly, where those channel/cavity openings locate. Here, the inner migration of ‘coke frontline’ is possibly driven by two forces: (1) as more catalytic sites (Brønsted acid sites) are needed for the dehydrogenation, and aromatization, coke gradually built up as the inner cavity/channel catalytic sites were fully occupied by the reaction; (2) coke formation is a condensation process, where geometry limitation has forced it to expand either towards to deeper cavity/channel space, or to the outside zeolite surface.

ELEMENT COUNT NOT MATCHED WITH 200 FILE - ELEMENT NAME Para In the above example [14], as the channel diameters of H-ZSM-5 are small and relatively uniform, there is not much internal space for the coke building up, whereas the larger inner cavity space allows the H-SAPO-34 to accumulate more coke species inside. It should be noted that the volume of coke storage here is not directly correlated with the coke capacity of zeolite. In contrast, due to the uniformly distributed channel size, H-ZSM-5 would possess a much higher coke tolerance capacity, this is because in principle, chemicals with larger than the channel diameter size are hardly formed inside [12, 13, 22, 25]. For H-SAPO-34, the smaller pore opening and much larger inner cavity make it difficult to move those internally formed large coke species to



**Fig. 2** Confocal fluorescence microscope images of H-ZSM-5 crystal during MTO reactions at 660 K with time-on-stream (*numbers* represent reaction minutes), achieved with laser excitation at **a** 488 nm (penetration 510–550 nm), and **b** 561 nm (penetration 565–635 nm), respectively, **c** Schematic representation of the H-ZSM-5 slice at which the confocal fluorescence measurements were performed, **d** Confocal fluorescence microscope images of

H-SAPO-34 crystal during MTO reactions at 660 K with time-on-stream (*numbers* represent reaction minutes) achieved with laser excitation at 561 nm (penetration 565–635 nm), **e** Schematic representation of the H-SAPO-34 slice at which the confocal fluorescence measurements were performed. Referenced from the works by Mores et al. [20]

outside space, thus eventually leading to an irreversible catalyst deactivation [10, 12, 13, 34–36].

### Coke accumulation in large pores over the zeolite surfaces

As discussed above, we would anticipate a large proportion of cokes are selectively built up and dispersed on the zeolite surface, without any geometry limitations, and these are most favourable for the growth of coke clusters and particles. Therefore, while the coke growth moves inward to the zeolite inner space, it would also concomitantly spread onto the outside zeolite surface, possibly originating from the zeolite crystallite edges. Obvious questions originate from the fact that Brønsted acid sites—necessary for coke formation—are present in a greater portion inside the zeolite cavity/channels [33]. It is hard to confirm the catalytic behaviour of surface Si–OH (silanol) groups that are typical terminal structures of the zeolite framework, for their contributions to the reaction, as they only denote limited acid strength [10, 12, 13, 33]. However, considering there is a rapid mass transportation process during the reaction, the precursors of the external cokes are certain to be pre-activated inside the zeolite cavity/channels. Moreover, external cokes account for a great portion in the total coke amount, as reported by Bibby et al. [37]. They noticed that in a MTH reaction, the coke volume had exceeded the concomitant decrease in void volume; therefore, there must have been coke deposited over the external zeolite surfaces. Surprisingly, the estimated inner cavity cokes only accounted for about 20 wt% in the total coke amount.

Notably, the reaction rate and mass transportability also exert significant influences on the coke distribution in a porous zeolite system. In Fig. 3, coke formations via different reactant weight-hourly-space-velocities (WHSV) in a ZSM-5 zeolite are schematically represented, based on the work of Bibby et al. [5]. As illustrated in the bottom section of Fig. 3, H-ZSM-5 consists of two intersecting sets of channels, one straight, and another that has intersecting zigzag channels. These channels have different shaped openings that determine the shape selectivity observed in H-ZSM-5. One thing that should be taken into consideration is that although H-ZSM-5 catalysts are widely used in hydrocarbon conversions, they still possess a relatively low concentration of Brønsted acid sites, especially when the abundance of alumina is limited in the framework (typical Si:Al ratio > 10) [26]. As a large portion of Brønsted acid sites are located inside the zeolite channel, the reaction forefront gradually moves inwards to the inner channel space, which is driven by the reaction mechanism (Brønsted acid sites are essential for the catalysis). Therefore, we would presume there might be some coking sites arising from the initial reaction time at catalytic sites

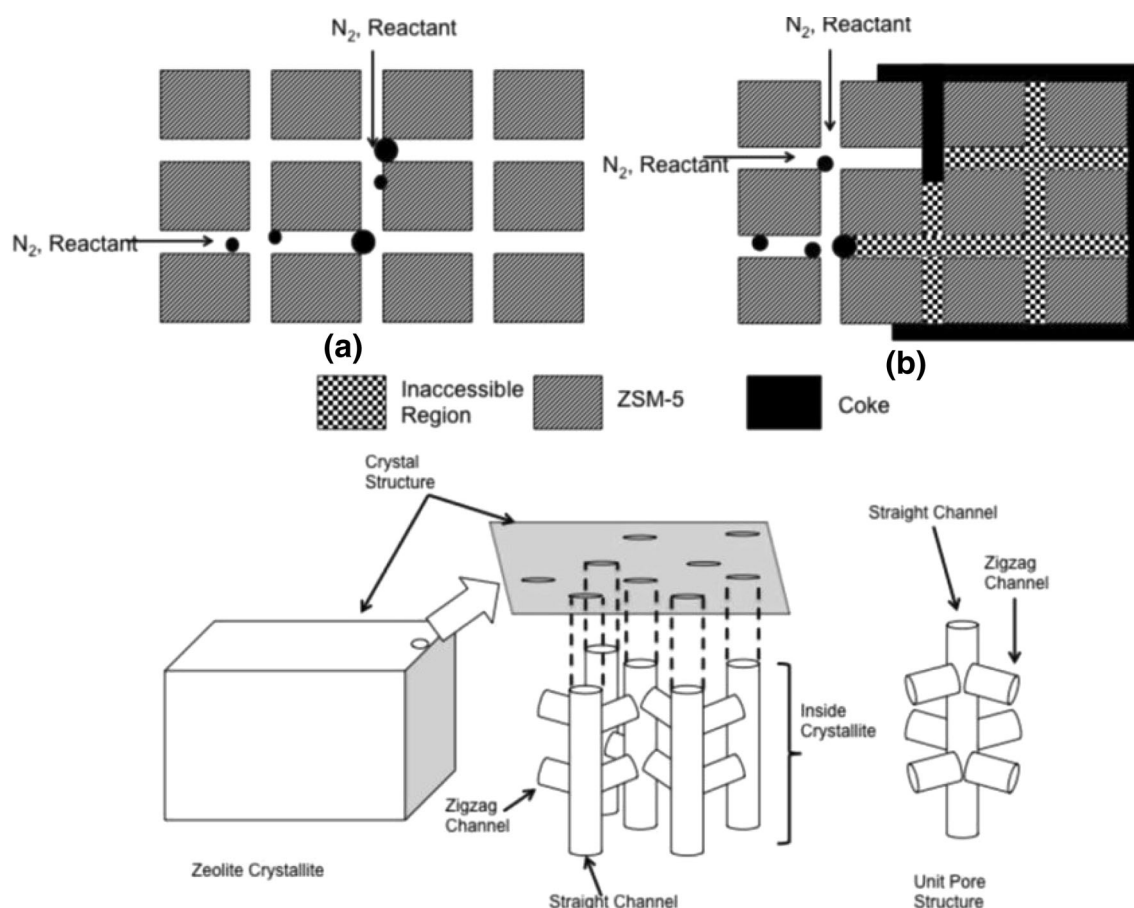
inside the zeolite channel, which is particularly the case when a lower reactant WHSV (the reactant feeding rate, e.g.,  $\text{WHSV} = 2 \text{ h}^{-1}$  means every 1 h, there are 2 g of reactant, e.g., methanol, flowed through 1.0 g of catalyst, this is also known as the reaction duty for the catalyst) [38]. When the reaction is further speeded up possibly due to the increased reactant feeding rate (a higher HSV), there will be an accelerated coke formation, most likely attributed to enhanced product accumulations. Here the zeolite edge areas that have the first contact with the reactants again plays an important role, where the product accumulation is often selectively faster, further limiting the internal migration of the reactants to more inner areas. The initially accelerated product accumulation at zeolite edges (near the channel openings) makes the inner catalytic sites gradually isolated from the reaction, and finally stops the reaction by forming an ‘envelope’ of coke species that cover the whole zeolite body. Normally the zeolite channel openings are positioned vertically to the zeolite crystallite surface, which can be somewhat described as a ‘honeycomb’ structure, and this further leads to a potential rapid blocking effects by the coke species deposited onto the zeolite surfaces.

### Proposal as to the chemistry leading to coke formation on the zeolite surfaces

Coke formation starting at the zeolite edges is further confirmed in the work of Nordvang et al. [39]. The findings reveal that fast formation of aromatic molecules at periphery of the H-ZSM-5 crystals is the main reason for the coke coverage over the zeolite body, which is converted into more deeply dehydrogenated, further condensed, larger sized poly-aromatics that are the main component of cokes in hydrocarbon conversions.

We envisage the building up of aromatics (e.g. methylbenzenes), and subsequent poly-aromatics formation as well as the resulted extension of superficial carbonaceous structure, finally reaching a ‘network’ of carbons, are the most contributing factors and processes in the external coke deposition. As a result, the reaction is stopped by the inhibited mass transportation owing to the reduced number of accessible zeolite channel openings. Instead of a monolayer of carbons, coke accumulation over a zeolite surface is almost certain to be a multi-layer formation, where the growing ‘networks’ of carbons are structurally built up as the reaction moves forwards, and finally a ‘pre-graphite’ status could be achieved [1]. Notably, owing to the thermodynamics effect and the reaction mechanism [12, 13, 40], dehydrogenation is unavoidable for most of the hydrocarbon products deposited in the system. As a result of this, more  $\text{sp}^2$  carbons are formed due to the loss of hydrogen. Straight chain structures, such as aliphatic, or





**Fig. 3** Schematic representation of a H-ZSM-5 structure, showing the channel structures of a MFT topology, and the channel openings vertically positioned to the zeolite crystallite surfaces (*bottom*); and the coke depositions in the MTH reaction over H-ZSM-5, when a

lower reactant feeding rate (a low GHSV) is employed (*left*), also the case that a higher reactant feeding rate (high GHSV) is employed. The reactant is assumed to be carried with the  $N_2$  gas into the system. Taken from Bibby et al. and Guisnet et al. [1, 4, 5, 13]

chain-olefin hydrocarbons in which  $sp^3$  carbons dominate are continuously consumed, and converted into the  $sp^2$  carbonaceous compounds [1, 12, 13, 39, 41]. Nevertheless, layers of hex-atomic ring structure are favored in the above discussed chemical processes, and often the graphitized coke plays a terminal role in most of the reactions [1].

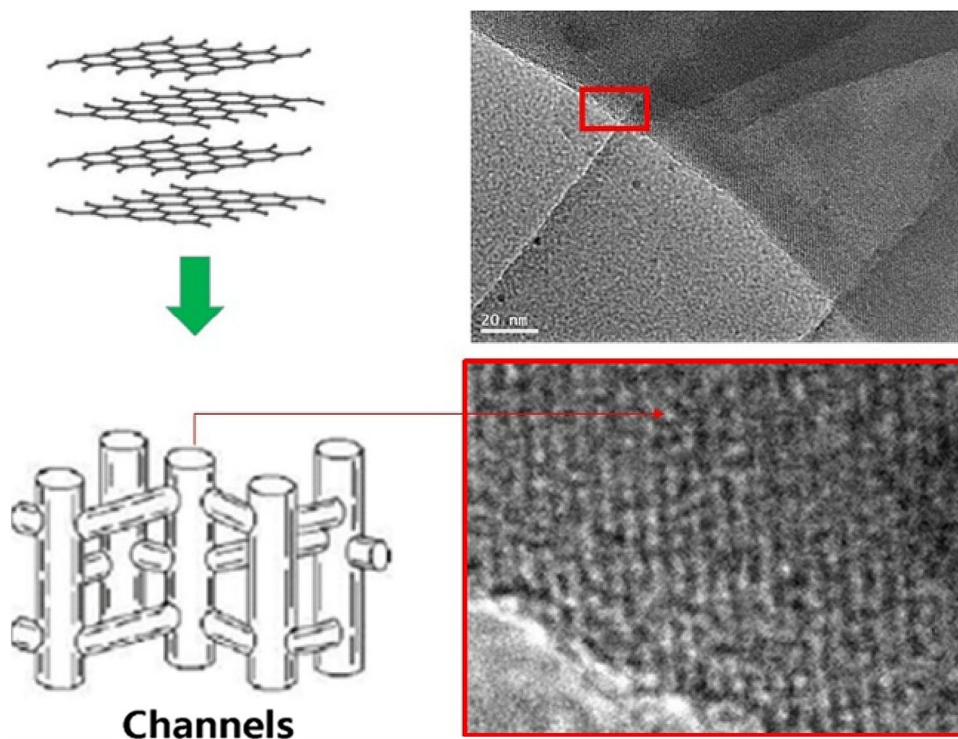
This transmission electron microscopy (TEM) measurements were undertaken in our lab using JEM-3000F microscope (300 kV). The catalyst samples were dispersed in ethanol and baked out in vacuum after transferring onto the carbon-coated copper grids. This is from our experimental results.

Additionally, we should not ignore the role of small fractions of light hydrocarbons, e.g. the light olefins with a much higher transportability in the reaction, for their contribution to the poly-aromatics formation. A large number previous studies have already observed the conversion of olefins into methyl-benzenes, e.g. xylene, at the zeolite external surface [42], and those mono-ring aromatics are the basic units to yield a poly-aromatic structure.

The MTH mechanism also implies the potential function of olefin aromatization in the coke formation, as the relevant chemical processes are greatly thermodynamically favoured under the reaction conditions [1, 12, 13, 21, 25, 39–41]. Therefore, a comprehensive view of coke formation over zeolite surface would involve both catalytic cycles in the dual-pathway MTH mechanism (Fig. 1), although the olefin based hydrocarbon pool may plays a less important role in most cases.

The coke build-up in terms of layered poly-aromatics (graphite carbons [1]), most possibly positioned vertically and covered the ZSM-5 zeolite channel openings, is presented schematically in Fig. 4. Here we also show TEM images of a coke-covered post-run industrial H-ZSM-5 (micrometer crystallite size, Si/Al = 25, Wenfeng, Beijing, China), obtained from MTH reaction via conditions of 673 K, atmosphere pressure, WHSV of  $2\text{ h}^{-1}$  and reacted for 300 min. The presence of superficial carbonaceous species is reflected by the black zones, which were originally transparent in the zeolite crystallites. The amplified

**Fig. 4** Schematic representation of layers of carbon structure (graphitized) building up over the zeolite surface, in a vertical position over the zeolite channel openings based on a TEM images of a coked industrial H-ZSM-5 zeolite (Si/Al = 25, micro-sized crystallite), reacted in MTH reaction under the conditions of 673 K, atmosphere pressure, WHSV of  $2 \text{ h}^{-1}$ , and reacted for 300 min



vision of selected areas shows clearly pore blockings at the zeolite edges. Notably, the accumulation and evolution of coke species, mainly made up of poly-aromatics originating from smaller, single-benzene-ring aromatics have been studied and monitored in the early UV-Raman coke studies [43, 44].

## Conclusion

Coke accumulation in methanol-to-hydrocarbon reaction over acidic zeolite proceeds at both the internal and external cavity/channel surface, but most notably at the zeolite surfaces. Initial coke building up may be initiated at the zeolite edge sites, where the reactant comes into first contacts with the active catalytic sites. The process is stimulated and catalysed by the rapid formation of aromatics, which are then converted into the network of poly aromatics, the precursor of carbon deposit, resulting in the formation of the blockage of graphite carbons. While poly-aromatics are still the major components of the external cokes outside of the zeolite pores, non-aromatic species are also coke precursors and have contributed to the coke accumulation via series of aromatization.

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