

# Ultra-short contact time conversion of chloromethane to olefins over pre-coked SAPO-34: direct insight into the primary conversion with coke deposition†

Yingxu Wei,<sup>a</sup> Dazhi Zhang,<sup>a</sup> Fuxiang Chang,<sup>a</sup> Qinghua Xia,<sup>ad</sup> Bao-Lian Su<sup>\*abc</sup> and Zhongmin Liu<sup>\*a</sup>

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**Hydrocarbon species trapped in the catalyst that work as the reaction center and govern the conversion and product selectivity of chloromethane transformation were revealed by a very efficient home-made ultra-short contact time pulse reaction system over pre-coked SAPO-34.**

The methanol-to-olefins (MTO) process has been successfully developed as an applicable route in the production of light olefins from abundant natural gas or coal reserves.<sup>1</sup> A parallel process, the conversion of methyl halides (such as CH<sub>3</sub>Cl) to higher hydrocarbons, has also been studied in the past 20 years,<sup>2</sup> and found to be a very efficient and promising alternative for lower olefin production.<sup>2–6</sup> Two important distinctions have been noticed, *i.e.* the chloromethane conversion does not produce dimethyl ether as is usually present in the MTO process but generates hydrogen chloride as one by-product. Since the above-mentioned reactions are performed over the same zeolite catalyst, giving rise to similar distributions of hydrocarbon products, similarities in both reaction mechanisms have been expected.<sup>3</sup> Considerable efforts have led to more than 20 distinct MTO mechanisms and reveal a general agreement on the MTO process, *i.e.* the MTO reaction proceeds *via* an indirect pathway with a so-called “hydrocarbon pool” reaction center.<sup>4</sup> However, to date, the mechanism of CH<sub>3</sub>Cl transformation over zeolites or SAPOs, supposedly comparable to the MTO reaction, is less known.

SAPO-34 is the most active and selective catalyst developed for the MTO process.<sup>5</sup> In the MTO process, coke species are responsible for catalyst deactivation by poisoning active sites and blocking pores.<sup>7</sup> Coke also behaves as an important

reaction center for olefin assembly over a working catalyst.<sup>4</sup> For chloromethane transformation, an FTIR study has shown an enhanced conversion rate, promoted by deposited aromatic species.<sup>6</sup> However, some questions usually discussed in the MTO mechanism, such as induction period and intermediate species, are still less conclusive in the chloromethane transformation. This is due to the fact that it is difficult to distinguish the products of primary conversion from those that undergo a secondary transformation. In this work, a home-built pulse reaction system<sup>8</sup> is used to clarify the reaction of halogenated methane on a series of pre-coked SAPO-34 (Si<sub>0.11</sub>P<sub>0.41</sub>Al<sub>0.48</sub>O<sub>2</sub>) catalysts (Table S1, ESI†) and to obtain more information on the primary products. Reactant feeding is conducted *via* injection, allowing an ultra-short contact time between reactant and catalyst (2.4 ms in the present study) to eliminate the secondary interconversion of olefin products as much as possible and to facilitate a direct observation of the primary transformation. The volatile products behind the catalyst bed are directly analyzed by an on-line chromatograph. The present work provides new, as yet undiscovered, information on the formation of the primary products and the chemical composition of the hydrocarbon pool. These are essential for understanding the reaction mechanism of chloromethane transformation and the role of coke deposition and evolution on catalyst performance. This is also of great importance for the development of highly efficient catalysts for light olefin production.

Fig. 1 highlights how the amount of coke species plays a role in CH<sub>3</sub>Cl conversion, where the chloromethane pulse (*ca.* 0.28 mg) was injected into a fresh or pre-coked SAPO-34 bed. As compared with continuous flow reactions,<sup>6</sup> the ultra-short contact time (*ca.* 2.4 ms) herein leads to a lowered chloromethane conversion. The lowest CH<sub>3</sub>Cl conversion (0.35 wt%) is obtained over the fresh catalyst, revealing poor activity of the catalyst as the short contact time means few coke species have formed. Prior coke deposition on the catalyst (coke amount of 0.60–1.06 wt%) gives rise to a predominant enhancement of CH<sub>3</sub>Cl conversion. The conversion on the catalyst with 0.60 wt% coke deposition is 20 times that of the conversion on the fresh catalyst. When the coke amount lies in the range of 1.06–2.49 wt%, the conversion remained at a high level. Whereas for the severely coked catalyst (>3 wt%), a marked decline in conversion, caused by deactivation, is observed.

In the continuous flow transformation of CH<sub>3</sub>Cl on SAPO-34 catalysts, light olefins (ethylene and propylene) are

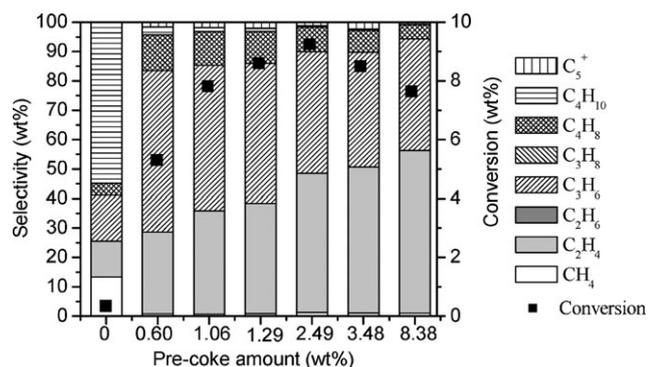
<sup>a</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P. O. Box 110, 116023 Dalian, P. R. China. E-mail: liuzm@dicp.ac.cn; Fax: +86-411-84691570; Tel: +86-411-84685510

<sup>b</sup> Laboratory of Inorganic Materials Chemistry (CMI), The University of Namur (FUNDP), B-5000 Namur, Belgium. E-mail: bao-lian.su@fundp.ac.be; Fax: +32-81725414; Tel: +32-81724531

<sup>c</sup> State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 430070, Wuhan, Hubei, P. R. China

<sup>d</sup> Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University, 430062 Wuhan, P. R. China

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**Fig. 1** Catalytic performance evolution with pre-coke variation. Conditions: 723 K; catalyst, 8.9–10.1 mg;  $\text{CH}_3\text{Cl}$ , 0.28 mg/pulse; contact time, 2.4 ms.

the dominant products.<sup>6</sup> But when chloromethane is fed into the fresh SAPO-34 bed by injection, among the trace volatile hydrocarbon products (970 ppm yield), ethylene and propylene form whilst methane and butanes are more predominant, indicating the low efficiency of the fresh catalyst in transforming  $\text{CH}_3\text{Cl}$  to olefins. These behaviours are in line with the characteristics of the kinetic induction period in the MTO process.<sup>9</sup> For comparison, the pulse experiment of methanol conversion was also conducted on the fresh SAPO-34 bed under almost identical conditions. Even at ultra-short contact times (2.1 ms), methanol conversion reached 64 wt% without an evident induction period (Table 1), in which the selectivity of propylene and ethylene was around 53% and 16%, respectively, amongst the hydrocarbon products. This implies that the induction period duration varies with reactant. Under the present reaction conditions, the induction period of MTO could almost be eliminated in one pulse duration (2.1 ms), but it is prolonged when using chloromethane as the reactant. The slow kinetics are possibly related to the lower reactivity of methyl halides compared with methanol.<sup>10</sup>

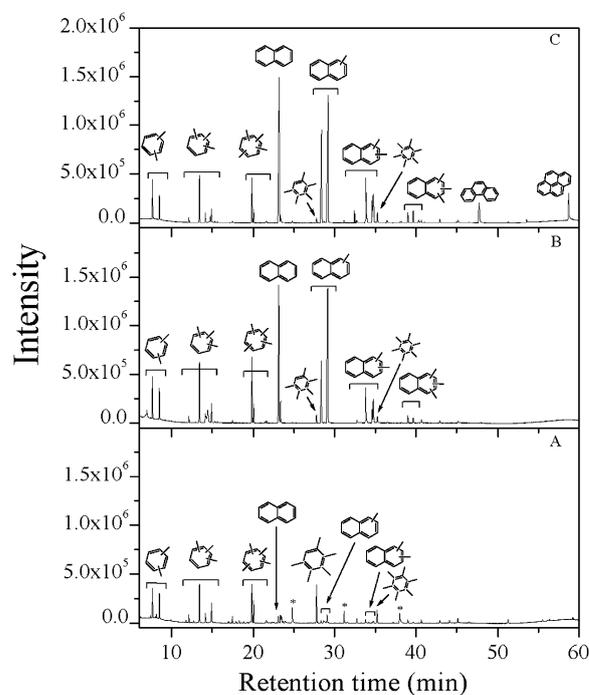
Detailed product analysis shows that prior coke deposition strongly favours the synthesis of olefins in chloromethane conversion. The performances with enhanced conversion and olefin selectivity are similar to the reaction characteristics of MTO at a steady-state stage over a working catalyst. The amount of coke on the catalyst influences the selectivity of light olefins. For example, propylene selectivity is high on the SAPO-34 with less coke deposition (coke amount < 1.29 wt%), but declines stepwise with increasing coke deposition.

**Table 1** Methanol conversion and product selectivity over fresh SAPO-34 at an ultra-low contact time (2.1 ms)

Methanol conversion (%)	63.73
Product selectivity (%)	
Methane	4.85
Ethylene	16.43
Ethane	0
Propylene	52.86
Propane	0
Butenes	16.56
Butanes	1.50
C5+	7.79

Meanwhile, the increase in coke amount leads to the gradual increase in ethylene concentration in the effluent stream. HCl appears in the products, but no Cl-containing hydrocarbons are detectable.

The compounds trapped in the pre-coked catalyst were collected by dissolving the catalyst in HF solution and extracting them with a mixed solution (1:3) of  $\text{CCl}_4$  and  $(\text{CH}_3\text{CH}_2)_2\text{O}$  then analyzed by GC-MS (Agilent 6890/5973N MSD) with an HP-5 column. Fig. 2 compares the GC-MS chromatograms of the extracted hydrocarbons. Noticeably, the pre-coke deposition of 1.06 wt% can eliminate the induction period. The organic components extracted from this sample are dominated by polymethyl benzene (Fig. 2A). This result is in agreement with the hydrocarbon pool mechanism, proposing multi-methyl substituted benzene as the major reaction intermediates.<sup>4</sup> For the slightly-deactivated catalyst (Fig. 2B), multi-methyl substituted benzene and naphthalene are predominant. The abundance of naphthalene and naphthalene derivatives increases further in the extracts from a severely coke-deposited catalyst (Fig. 2C). The appearance of phenanthrene and pyrene means that the voids in the pores of the catalyst are partially filled with polyaromatics, which contributes to the serious deactivation caused by greatly reduced mass transport of reactants and products. The evolution of the trapped coke species corresponds to the distribution of olefin products. The generation of propylene and ethylene is favoured by the deposition of multi-methyl substituted benzenes. With the appearance of naphthalene derivatives or even larger polyaromatic coke species, ethylene selectivity increases because of pore modification by coke species. The pore modification by coke deposition has been well evidenced by  $\text{N}_2$  adsorption measurements (Table S2, ESI<sup>†</sup>).



**Fig. 2** GC-MS chromatograms of extracts from pre-coked SAPO-34 with coke amounts of 1.06 wt% (A), 4.43 wt% (B), 6.97 wt% (C).

Note that Cl-containing hydrocarbons are also not detected by GC-MS from the extracted compounds.

In summary, the results collected in this study indicate that chloromethane conversion is governed by the trapped hydrocarbon species. The induction period with inefficient chloromethane conversion can be eliminated by coke deposition. Coke species accommodated in the cage of SAPO-34 work as critical reaction centers and are responsible for the production of olefins. The hydrocarbon pool mechanism proposed for the MTO process can also be utilized to explain the synthesis of olefins from halogenated methane. The generation of HCl by-product does not exert an apparent effect on the yield of olefins over SAPO-34. Compared to the conversion of methanol on SAPO-34, the chloromethane reaction with a prolonged induction period facilitates the direct observation of primary transformations.

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