

Methyl Halide to Olefins and Gasoline over Zeolites and SAPO Catalysts: A New Route of MTO and MTG

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Abstract: Rational and efficient conversion of methane to more useful higher hydrocarbons is one of the most important topics of natural gas utilization. Although methane activation and its conversion to valuable compounds attract an increasing attention, methane conversion is often made in indirect way through the very energy-consuming step for syngas production from steam reforming of methane. Some promising results appeared to be of significance for the development of an alternative and potential route for the production of high value-added products from methane. Efficient conversion of methane to higher hydrocarbons could be realized via methyl halide as the intermediate. After the production of halomethane, they could be transformed to gasoline and light olefins over modified zeolites and SAPO molecular sieves. High conversion efficiency and selectivity indicated the feasibility of industrial application. The research gained recently growing interest from the point of view in both fundamental research and industrial application. The study on the reaction mechanism shed light on the possible route of C–C bond construction from methyl halide, which is the very important issue of the C₁-reactant conversion to higher hydrocarbons. Hydrogen halide generation during methyl halide conversion did not exert apparent impact on the reaction mechanism and the structure stability of the catalysts. This review deals with the evolution of the field and comments the advantages to be explored and the drawbacks to be prevented for the development of new and sustainable methane-to-olefins (MTO) and methane-to-gasoline (MTG) routes via methyl halides.

Key words: methyl halide; hydrocarbons; zeolite; SAPO-34; reaction mechanism

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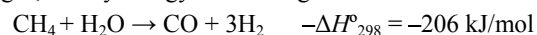
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Natural gas is a vital component of the world's supply of energy. Technologies in natural gas utilization and sustainable development draw an increasing attention from academy and industry. Efficient conversion of methane to higher hydrocarbons is one of the most important topics of natural gas utilization since 1980s and still remains a great challenge in energy sustainability in the future. The most successful processes for this conversion are still indirect ways. Methane is transferred by steam reforming to syngas, a mixture of CO, CO₂, and hydrogen, and the syngas can be converted to hydrocarbons (gasoline or olefins) using Fischer-Tropsch catalyst, or firstly to methanol using Cu/ZnO/Al₂O₃ catalyst and then to hydrocarbons with

methanol-to-olefins or methanol-to-gasoline catalyst [1–4]. Steam reforming, the dominant process for production of syngas, is very energy-consuming:



60% or more of the capital cost of GTL plants is associated with the reforming of methane to synthesis gas [5,6]. At the same time, even Fischer-Tropsch process has been proved to be an effective route for producing high hydrocarbons from syngas, the products always appeared in a large range. It is still difficult or even impossible, at least at the moment, to produce a single organic compound with high selectivity. The development of the process of MTO or MTG makes it possible to produce light olefins or the hydrocarbons in

gasoline range starting from natural gas [4]. The disadvantage of these routes is their complication of the conversion from methane to target products. From the economic point, the profit of the two routes depends on the price of methanol and usually the plant with large-scale methanol production is necessary. This also obstacles the utilization of natural gas in some area without big methanol plant. Since the difficulties mentioned above, research works have been still performed to search alternative routes for higher hydrocarbon production through methane transformation. Some promising results appeared in the work of catalytic conversion of methane to higher hydrocarbons via methyl halide as the intermediate. In this review, the state of the art of new MTO or MTG routes by the usage of microporous zeolites and SAPOs catalyst with advanced properties will be addressed.

1 From methane to higher hydrocarbons: the state of the art

In 1985, Nobel Prize Laureate, Olah and co-workers described a selective and very efficient monohalogenation of methane over supported acid or platinum metal catalysts [7]. Subsequent conversion of methyl halide into hydrocarbons employed bifunctional acid-base catalyst [8]. The most important advantage of this process established by Olah and co-worker is its high efficiency because the tetrahedral geometry of C atoms of methane is maintained and this is quite important for the construction of C–C bonds, while the steam reforming of methane concerns the complete destruction of methane to give other geometry of C atoms.

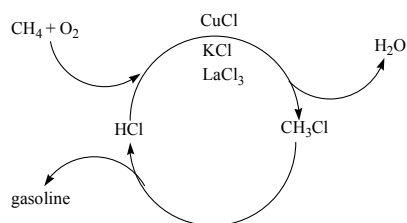
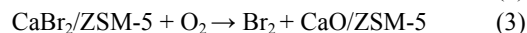
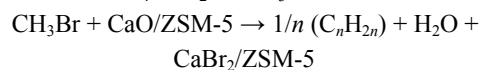
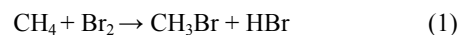


Fig. 1. The cycle process for the production of gasoline from methane via chloromethane as the intermediate.

In 1988, Taylor et al gave a cycle process for the production of gasoline from methane with chloromethane as the intermediate (see Fig. 1) [9]. The transformation from methane to gasoline combined two stages, which were based on the work of Pierre and Conner on the selective functionalization of methane for chloromethane production [10] and the result of Pieters et al. that the generated products of monosubstituted methanes over zeolite were independent of the substituent and depended only on the reaction condition for a given catalyst [11]. In the first stage of this process, methane, oxygen, and hydrogen chloride react over an oxyhydrochlorination (OHC) catalyst to produce

predominantly chloromethane and water; in the second stage, methyl chloride transfers to gasoline with ZSM-5 catalyst and HCl as the by product. HCl can be recycled for re-use in the OHC step.

Zhou and Lorkovic described the bromine-mediated process for the production of higher hydrocarbons through oxidative coupling of methane using O₂ as oxidant [12–18]. In the first step, CH₄ reacted with Br₂ giving a mixture of CH₄, bromomethane, and HBr, and then this mixture passed over a metal oxide supported zeolite catalyst which condensed bromo with 100% conversion to products, and neutralized HBr to form the metal bromide. In the third step, the supported metal bromide solid was treated with O₂ to generate Br₂ and supported metal oxide. The resulting product contained olefins and aromatics products with excess CH₄ and water.



All the three reactions ((1)–(3)) were proposed to be performed in one pot reactor and the reaction feeds were simply O₂ and CH₄. This coupling reaction predicted the possibility of direct utilization of natural gas in an integrated process. Selective bromination and reactor configurations, favoring comproportionation of methane and CH₂Br₂ or CHBr₃ to CH₃Br, are potential routes to improved carbon utilization of this process.

2 Catalysts for hydrocarbons formation from methyl halide

Methyl halide, such as chloromethane, can be produced through the OHC process [19–21] or monohalogenation of methane over supported acids or platinum metal catalysts [7] with the methyl halide selectivity exceeding 90%. Following step for the conversion of methyl halide to higher hydrocarbons has attracted much more research interest from academy and industry due to the significance of C–C bond construction from C₁-reactant. Intensive studies have shown that the direct conversion of methyl halide to higher hydrocarbons can be carried out on a series of acid zeolites like HZSM-5, HBeta, and HMOR and on cationic zeolites such as faujasites Y and ZSM-5 exchanged with mono or divalent cations [22–31]. Most of these work presented the product distribution in gasoline range from methyl halide conversion. In some recent studies, with the application of SAPO-34 molecular sieves, which has been proved to be the most excellent MTO catalyst, methyl halide could be transferred to hydrocarbons with extremely high selectivity for light olefins, such as ethylene, propylene, and butenes [32–43]. The structure of zeolites and SAPOs discussed in

this review is listed in Table 1. Among them, ZSM-5 and SAPO-34 were intensively studied in the open literatures and their structural features are depicted in Fig. 2. The structure of ZSM-5 possesses intersectant 10-member ring channel and SAPO-34 is characteristic of the narrow 8-ring pore opening and large supercages. A comparative study of chloromethane transformations were performed over zeolites and SAPOs by Zhang and co-workers and the results detailed in Table 2 indicated that the conversion and product distribution differed from the porous structure and acidity of the catalysts [34].

Table 1 Structural characteristics of zeolite and SAPOs for methyl halides conversion in this review

Catalyst	IZA code	Channel entrance	Channel diameter (nm)	Ref.
Beta	BEA	12	0.66 × 0.67 0.56 × 0.56	[27]
Y	FAU	12	0.74	[27]
ZSM-5	MFI	10	0.53 × 0.56 0.51 × 0.55	[22–28, 31, 34]
ZSM-35	FER	10–8	0.42 × 0.54 0.35 × 0.48	[34]
MCM-22	MWW	10	0.40 × 0.55 0.41 × 0.51	[34]
ZSM-34	OFF-ERI	8	0.36 × 0.51	[34]
SAPO-5	AFI	12	0.73	[34]
SAPO-34	CHA	8	0.38	[32–43]

2.1 Zeolite catalyst

In the cycle process proposed by Taylor and Noceti, ZSM-5 was applied in the conversion of methyl chloride to gasoline. Chloromethane was catalytically converted to higher hydrocarbons, including paraffins, isoparaffins, naphthenes, olefins, and aromatics over a zeolite catalyst of HZSM-5. The hydrocarbons in C₄–C₁₀ boiling range were the main products [9,22]. Long-term (>1000 h) studies were also been conducted to test catalytic ageing. Comparing the results with chloromethane and methanol as the feeds, the product distribution also proved that under the identical

condition over ZSM-5, both reactants, methanol or chloromethane would produce similar product distribution. Their trend over time was also similar.

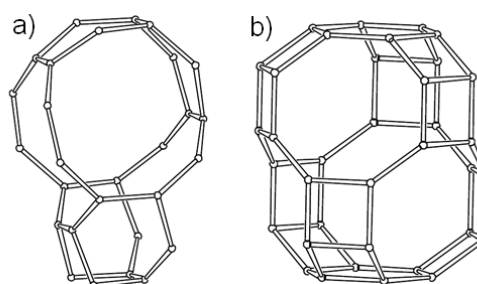


Fig. 2. Structural motifs of catalysts ZSM-5 (a) and SAPO-34 (b).

Lersch and Bandermann studied the chloromethane transformation over metal-exchanged zeolite ZSM-5 catalysts [23]. In their study, alkaline earth metal ions, such as magnesium, calcium, and barium ions, and some transition metal ions, such as silver, copper, chromium, zinc, nickel, cerium, cobalt, and manganese ions, were used for modification. The results indicated that the activity, selectivity, and lifetime of catalyst significantly depended on the cation used. Magnesium ion exchanged ZSM-5 exhibited the highest activity and stability. In an enlarged lab scale of 9 g catalyst loading, Mg-ZSM-5 showed a constant total conversion of chloromethane for about 25 h, while under the same condition, HZSM-5 deactivated completely with 24 h. They attributed the low coking rate of Mg-ZSM-5 to an improved selectivity to alkenes and a lower tendency to form aromatics compared to HZSM-5.

In the study reported by Sun and his co-workers, the emphasis was placed on maximizing the yield of light olefins, such as ethylene and propylene, from the reaction of chloromethane over modified ZSM-5 zeolite [24]. They found that the addition of Mg cation significantly improved the initial activity and lifetime of catalyst compared with the catalyst of HZSM-5 without modification; further modification with P was helpful for the lifetime of the catalyst and the selectivity of propylene. The characterization proved the roles of P and Mg²⁺ in decreasing Brønsted acidity of zeolite.

Table 2 Catalytic performance of chloromethane conversion to hydrocarbons over acid zeolites and SAPO catalysts [34]

Catalyst	T/K	X/%	Product distribution (%)										
			CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀	C ₅₊ ^a	Benzene	Toluene	Xylene
HY	400	44.82	1.51	13.23	0.38	3.48	9.24	0.92	25.29	25.00	—	19.72	1.22
HBeta	400	50.56	4.66	6.98	1.67	0.72	40.61	0.00	34.17	11.18	—	—	—
HZSM-5	400	99.93	0.70	1.51	0.73	1.66	24.80	0.95	19.41	23.91	2.28	9.52	14.55
HMCM-22	400	54.27	1.94	4.51	0.97	1.31	25.31	0.53	36.17	17.49	—	11.77	1.00
HZSM-35	400	45.02	0.58	12.09	0.20	14.06	3.47	19.16	4.85	32.80	1.90	8.75	2.15
HZSM-34	400	81.45	2.14	7.59	1.22	5.54	56.15	2.82	14.85	8.35	—	0.24	1.11
SAPO-5	450	20.19	3.16	9.08	0.22	31.46	3.66	14.00	6.47	30.68	0.30	0.36	0.60
SAPO-34	450	50.61	1.89	24.72	0.38	31.40	4.06	15.09	0.63	21.57	0.26	—	—

^aNot include BTX.

This modification provided an alternate pathway for reaction to occur with enhanced light olefins production. In the other work focusing on the conversion of chloromethane to light olefins [25], it was found that the selectivity to olefins increased with Si/Al ratio of ZSM-5, which was interpreted in terms of reducing hydrogen transfer, as the acid sites became more isolated. The exchange of Zn^{2+} cation increased the activity and selectivity to light olefins.

In Jaumain and Su's work, zeolites of Y-type, BETA, MOR, EMT, and ZSM-5 both in protonic and cationic forms were used as the catalysts in the chloromethane transformation to higher hydrocarbons [26–28] and the results are compared in Fig. 3. The catalytic conversion rate of chloromethane followed closely the acid strength in order of HBeta > HZSM-5 > HY [44,45]. The large pore zeolite catalysts, both in cationic and protonic form, such as Y, EMT, Beta, and MOR, in spite of their very interesting catalytic activity, led to the formation of large amount of coke in the chloromethane conversion due to the large size cages or channels present in these zeolites, while medium pore size ZSM-5 zeolite catalysts both in cationic and protonic form demonstrated their high activity and long life in the reaction and strong reduction in the coke formation. The detailed study of cationic ZSM-5 indicated that the conversion roughly followed the order of LiZSM-5 > NaZSM-5 > KZSM-5 > CsZSM-5. For product distribution, C_2 – C_6 hydrocarbons, such as ethylene, propane, butane isomers, aromatics, and HCl, were the major products. Catalyst aging tests showed that the most active zeolites were deactivated more quickly. The amount of coke formed decreased from LiZSM-5, NaZSM-5, KZSM-5 to CsZSM-5, which was attributed to less pore space available for the accumulation and formation of coke space in the framework exchanged with large cations.

Bromomethane conversion was less studied compared with the work of chloromethane. Modified ZSM-5 catalysts

were also applied in the conversion of methyl bromide to higher hydrocarbons [16–18,31]. PbO modification gave an enhanced selectivity for the production of aromatics. Over an active and selective catalyst of 5 wt% PbO/HZSM-5 ($SiO_2/Al_2O_3 = 70$), yield of aromatics was up to 31.6% at 360 °C [31].

2.2 SAPO-34 catalyst

Methyl halide conversion reported in early literature was usually performed over modified zeolites. The SAPO type molecular sieve catalyst, with excellent performance in catalytic conversion of methanol to light olefins [46], seemed to be neglected in methyl halide conversion until recently years. SAPO-34 has shown its superiority in the MTO process and could be therefore a very promising catalyst for methyl halide conversion to other hydrocarbons, especially to light olefins, such as ethylene and propylene, due to its small channel size.

SAPO-34 was employed as the catalyst for chloromethane conversion for the first time by Wei and co-workers [32] and presented high activity and selectivity for the production of light olefins [33–38, 41–43]. In the 350–500 °C temperature range, chloromethane was converted to ethylene, propylene, and butylenes with 70%–80% selectivity for C_2 – C_4 olefins (Fig. 4). Increasing reaction temperature increased conversion and enhanced the yield of lighter olefins [32].

Changing the Si incorporation or metal (Me = Mn, Co, Fe, Mg) modification of the SAPO framework gave variable performance of chloromethane conversion [35–38]. Based on the synthesis, characterization and catalytic tests of SAPO-34 with different Si incorporation, the correlations between Si content of SAPO-34 with framework element coordination, acidity and catalytic performance were established. More Si incorporation gave rise to $Si(nAl)$ ($n = 4-0$)

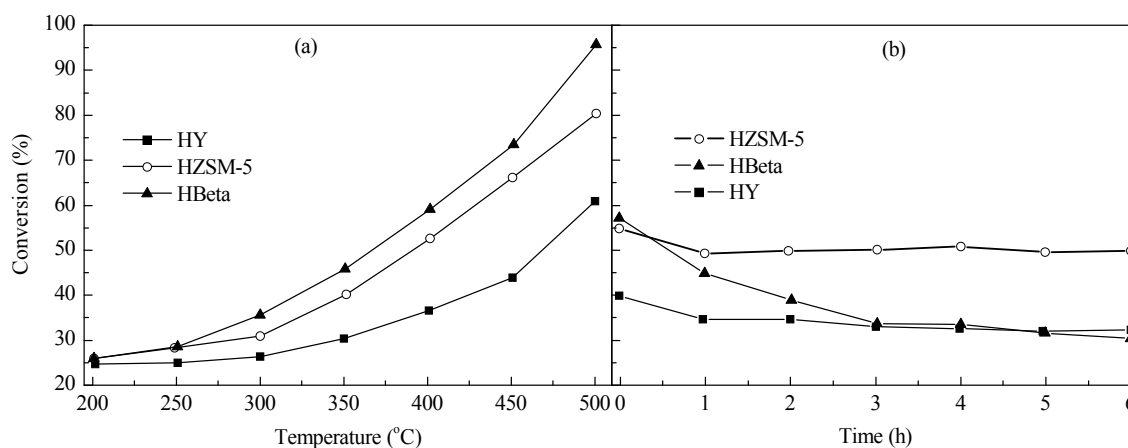


Fig. 3. Initial catalytic activity of chloromethane conversion on HY, HZSM-5, and HBeta zeolites as a function of temperature (a) and ageing test on these zeolites at 400 °C (b).

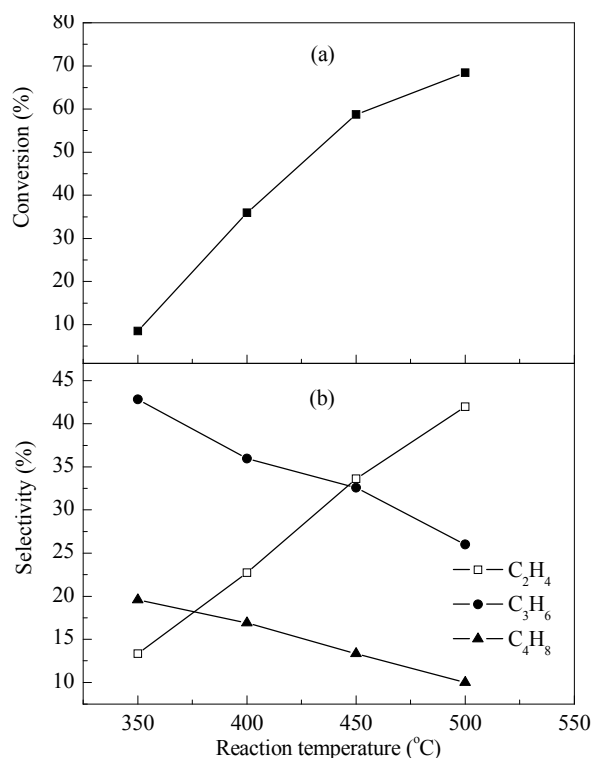


Fig. 4. Chloromethane conversion (a) and light olefins selectivity (b) over SAPO-34.

coordination states and stronger acidity. Higher chloromethane conversion and higher ethylene selectivity were obtained over SAPO-34 with high Si content ($\text{Si}/(\text{Al} + \text{P} + \text{Si}) = 0.10$). SAPO-34 with low Si content ($\text{Si}/(\text{Al} + \text{P} + \text{Si}) = 0.06$) and the only coordination state of Si(4Al) favored the propylene production and reduced coke deposition [35]. MeAPSO-34s (Me = Co, Mn, Fe) molecular sieves with the same CHA topology structure have been also synthesized and used as catalysts for chloromethane transformation to light olefins [36–38]. Catalytic performance proved that metal incorporation improved the catalyst life and favored the ethylene and propylene generation. The reactions performed over a series of MgAPSO-34s with various Mg stoichiometries indicated that Mg modification could efficiently lower the hydrogen transfer reaction level and contribute to the improved catalyst life and light olefin selectivity, in particular for propylene production. It was also found that the coexistence of metal species in the synthesis starting gel has effect on the Si substitution into AlPO framework. The ^{29}Si MAS NMR spectra in Fig. 5 indicated that, with more metal incorporated into the framework, Si island predominant formed and caused lowered acid density of MeAPSO-34 [37].

A relevant work published by Svelle and co-workers in 2006 reported methyl chloride and methyl bromide conversion over SAPO-34 catalyst [41]. Figure 6 gives the MeBr conversion versus time on stream at 300–450 °C and product

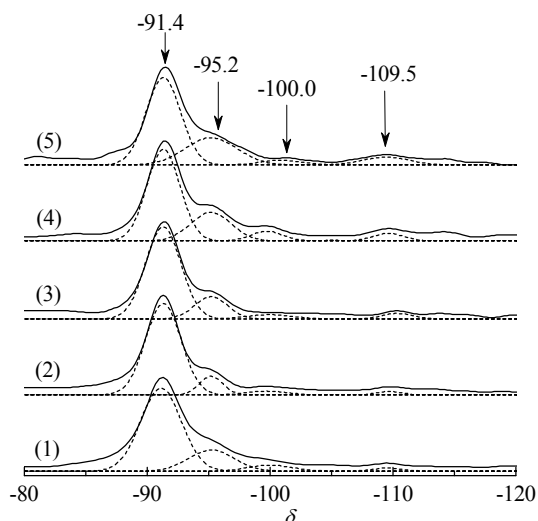


Fig. 5. ^{29}Si MAS NMR spectra of as-synthesized MgAPSO-34 with Mg content (wt%) of 0 (1), 0.33 (2), 0.35 (3), 0.83 (4), and 1.65 (5).

uct selectivity at 450 °C. Comparative experiments were performed using methanol to elucidate whether the activity of reactant could change the product selectivity over an identical catalyst. The conversion levels of methyl chloride and methyl bromide were similar, whereas that of methanol was 25 times higher. Reaction temperature had effect on the

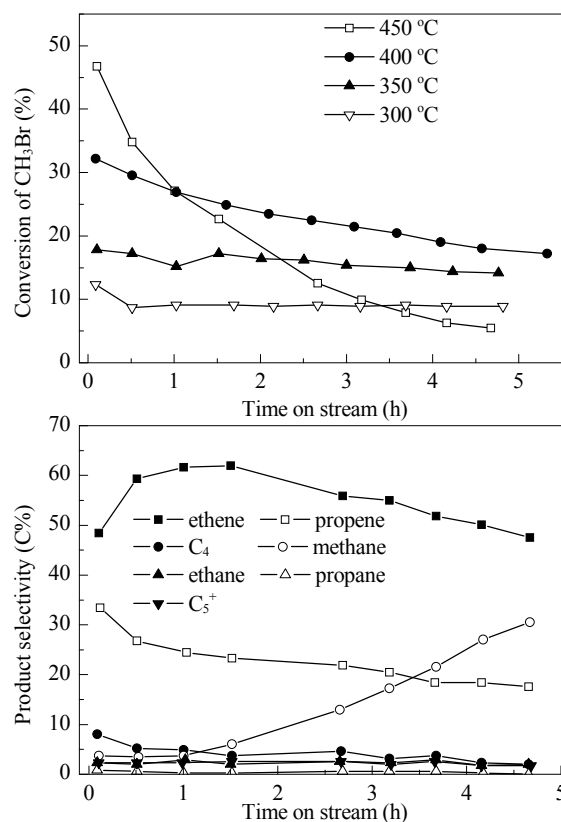
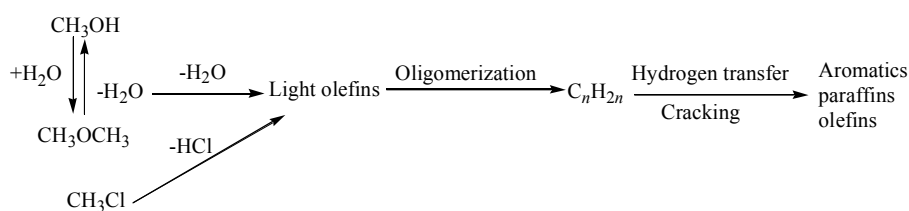


Fig. 6. MeBr conversion versus time on stream at 300–450 °C and product selectivity at 450 °C



Scheme 1. Conversion of methanol or chloromethane to higher hydrocarbons.

stability of catalysts on stream, highest initial conversion appeared at 450 °C while the conversion declined with prolonged reaction time. Low temperature reaction presented the stability in catalytic performance. Reaction-regeneration cycles at 450 °C indicated that SAPO-34 catalyst was an active, selective, and structurally stable catalyst for the conversion of methyl chloride to olefins. The effect of CH_2Cl_2 impurities on the conversion of CH_3Cl to olefins over SAPO-34 was also investigated. CH_3Cl was co-reacted with CH_2Cl_2 in a 10:1 ratio at 400 °C over a SAPO-34 catalyst. CH_2Cl_2 addition promoted the formation of aromatic compounds and led to rapid deactivation of the catalyst in the CH_3Cl conversion to olefins [42].

3 Mechanism investigation: C–C bond formation from methyl halide

The fundamental study of MTO or MTG process in the past 30 years produced at least 20 different mechanisms, such as oxonium ylide, carbene, carbocationic, free radical, and hydrocarbon pool [46–49]. There are undoubtedly many parallels between the reactions of methyl halides and methanol transformation to higher hydrocarbons. The main reaction steps of the methanol conversion to hydrocarbons can be summarized as Scheme 1.

The important distinction between methyl halides and methanol transformation maybe that the proposed intermediates derived from CH_3OH , such as CH_3OCH_3 , are not accessible from methyl halide.

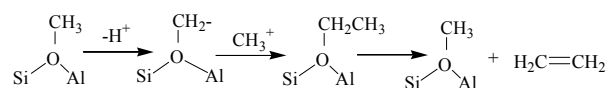
Accompanying the study of the transformation of methyl halide to higher hydrocarbons, some reaction mechanisms were also proposed. Earlier studies suggested the first C–C bond formation from methyl halide through the methylation of framework bonded CH_2 group [27–30], while later work over SAPO-34 indicated methyl halide conversion to higher hydrocarbons possibly followed indirect way as methanol

conversion [49–51].

3.1 Direct route of C–C bond formation

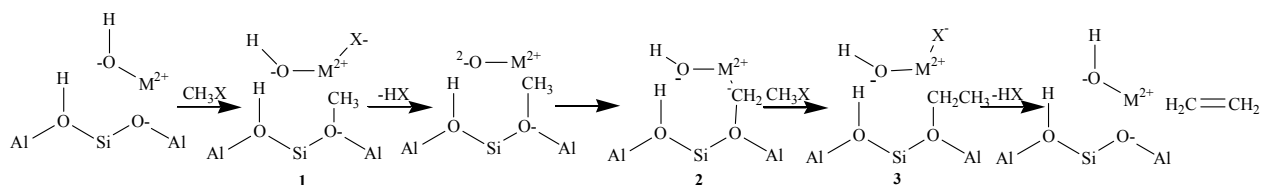
Murray and his co-workers studied the conversion of methyl halides to hydrocarbons on basic zeolites, including alkali metal and divalent metal exchanged zeolites [29,30]. In their work of in situ ^{13}C MAS NMR study, the conversion of methyl iodide on zeolite CsX was proposed to proceed through a framework-bound methoxy intermediate over CsX; and an analogous framework-bound ethoxy species also easily formed upon adsorption of $\text{CH}_3\text{CH}_2\text{I}$.

A mechanism proposed for methanol conversion to alkene or aromatics [52] was employed by Murray to explain the conversion of alkyl iodides on CsX (Scheme 2). A framework methoxy group formed from nucleophilic attack by the framework site, possibly with the assistance of Cs^+ cation in the removal of the halide leaving group; the species was assumed to be deprotonated by another basic framework site. At the same time, a second methyl halide was polarized by a Lewis acid-base interaction to form CH_3^+ for methylation of the methoxy group. The first species with a C–C bond was proposed to be framework-bound ethoxy group, which quickly eliminated ethylene [29].



Scheme 2. Methyl halide conversion on CsX [29].

In the study of methyl halides reaction on bivalent metal-exchange zeolite catalysts, Murray and their coworker proposed a detailed mechanism for this reaction and also described an explicit role of the metal [30]. With FT-IR and ^1H MAS NMR, they determined the nature of the active sites of the divalent metal zeolite, such as ZnZSM-5, and proposed a modified mechanism shown in Scheme 3. This



Scheme 3. Methyl halide conversion on divalent metal-exchanged zeolite [30].

mechanism proposed three intermediate species containing carbon, all of them bound to the zeolite framework and one of them also stabilized by the metal. The methoxy species as species 1 had been proved in his study discussed above [29]. The species 2, framework-bound CH_2 species as the second intermediate, was speculated to form during the key step of hydrocarbon synthesis. This species was generated from deprotonation of methoxy species and was also stabilized by the metal available, such as Zn or Mg in the study. The final intermediate, the framework-bound ethoxy as species 3 was the first species with C–C bond in the conversion from methane halide to olefins.

In the work of Sun and co-workers [24], chloromethane was transferred to ethylene and propylene over Mg-ZSM-5 and P-Mg-ZSM-5. He proposed the ethylene formation via the following route: Mg^{2+} was involved in the activation of CH_3Cl , which was same as the first intermediate formation in the mechanism proposed by Murray [30]; While for C–C bond formation, Sun gave different opinion that C–C bond was generated via the addition of carbene intermediate to the surface methoxy group. With the elimination of this group, ethylene formed.

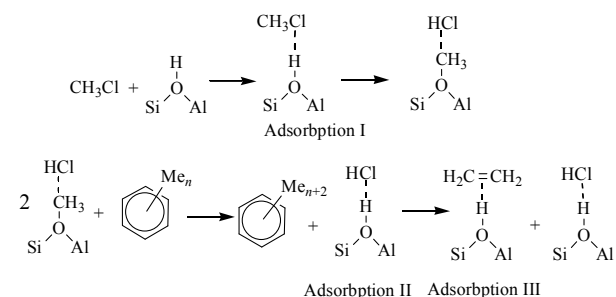
Jaumain and Su [27,28] studied the mechanism of chloromethane conversion over NaZSM-5 to higher hydrocarbons by in situ FT-IR. Chloromethane adsorption happened at room temperature, but no conversion occurred. With the increase of temperature, vibrations, characteristic of higher hydrocarbons ($-\text{CH}_2-$ stretching and bending, $\text{C}=\text{C}$ stretching and deformation) were detected at 400°C , indicating that C–C bond formation occurred and higher hydrocarbons were produced. The creation of new hydroxyl species was also found during the conversion, with the absorbance at 3230 , 3500 , 3595 , and 3672 cm^{-1} . They attributed the new hydroxyl generation to the interaction of framework oxygen atoms with HCl as a product of the conversion. They proposed that, in the first step of the conversion, dehydrohalogenation occurred on NaZSM-5 with the dissociation of CH_3Cl and the adsorbed species of chloromethane was transferred to methoxy species over zeolite surface, which was widely accepted as the intermediate of chloromethane to higher hydrocarbon. The first C–C bond formation occurred via a carbene transfer between neighboring methoxy group. The C–C link was formed by the carbene insertion in C–H bond of a methoxy group. From the first insertion, other insertions can occur and increased the chain length.

Comparing reaction mechanisms for C–C bond formation given by Su and Murray [27–30], both of them regarded methoxy species as the first intermediate, carbene generated from methoxy species as the second intermediate, and the final ethylene came from an ethoxy species. The differences between them was that in Murray's work, the formation of C–C bond came from the methylation of framework-bound

CH_2 species with a methyl group from dehydrohalogenated CH_3X [29]; while the CH_2 species in Su's mechanism would be more free and can transfer from one framework site to the neighboring methoxy group and C–C bond formed from the carbene insertion in C–H bond of the neighboring methoxy group [28]. The two above-mentioned mechanisms were considered to be the direct routes for C–C bond formation.

3.2 Indirect route of C–C bond formation

The catalytic performance with efficient conversion and high light olefins selectivity proved that SAPO-34 was very excellent catalysts for the transformation of methyl halide to light olefins [32–42]. Methyl chloride conversion over acid catalyst SAPO-34 was also studied with in situ FT-IR [33,39] and three shifts of $\text{Si}(\text{OH})\text{Al}$ caused by three interaction between hydroxyl group and adsorbed species of reactant and products, such as chloromethane, alkenes and HCl, were detected. Based on the FT-IR observations combined with the catalytic test results, Wei and coworkers proposed a realistic reaction mechanism. A possible way of C–C bond formation from methyl chloride conversion is given in Scheme 4. The first reaction center, such as methylbenzene was assumed to be present in the cage of SAPO-34, which may come from the initial building-up with methoxy species or trace coke deposition from incomplete calcinations [53]. Subsequent methylation from the adsorbed chloromethane led to the formation of polymethylbenzenes and HCl, and then the polymethylbenzenes eliminated an ethylene molecular. Once ethylene was synthesized, additional methylbenzenes would continue to form through oligomerization and cyclization of olefins followed by hydrogen transfer. Since the SAPO-34 processes the structure of supercage and narrow 8-ring pore opening, the aromatic products, benzene or substituted benzene, cannot escape the narrow window of SAPO-34, and could not be detected by the on line gas chromatography, while the appearance of absorbance at 1572 cm^{-1} , which could be attributed to $\nu(\text{C}-\text{C})_n$ of aromatic species, indicated the reaction center formation as have been proved by previous work



Scheme 4. Adsorption and conversion of chloromethane over SAPO-34.

[54–56].

A further study of chloromethane conversion over a pre-cooked catalyst using a pulse reaction system allowing a very short contact time showed that hydrocarbon pool species, such as methyl substituted benzenes or naphthalenes trapped in the SAPO-34 catalyst worked as the reaction center and governed the conversion and product selectivity (Fig. 7) [40]. The induction period with inefficient chloromethane conversion was detected and could be eliminated by coke deposition. Coke species confined in the cage of SAPO-34 worked as critical reaction centers and were responsible for the production of olefins. The hydrocarbon pool mechanism [54,55] proposed for the MTO process can also be utilized to explain the synthesis of olefins from halomethane. The generation of HCl by-product did not exert an apparent effect on the yield of olefins over SAPO-34. Compared with the conversion of methanol on SAPO-34, the chloromethane reaction presented a prolonged induction period, which facilitated the direct observation of the primary transformations.

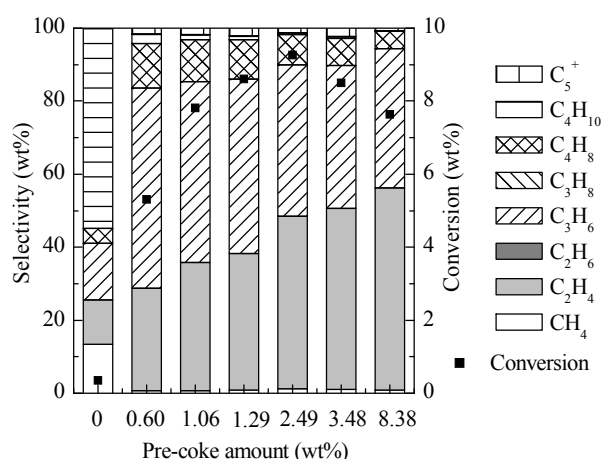


Fig. 7. Catalytic performance of chloromethane conversion over SAPO-34 with pre-coke variation. Reaction conditions: 723 K, catalyst 8.9–10.1 mg, 0.28 mg/pulse CH₃Cl, contact time 2.4 ms.

In the Svelle's study, methyl chloride and methyl bromide conversion to hydrocarbons over an SAPO-34 catalyst was studied and compared with methanol conversion [41,42]. The induction period could be overcome by adding a small amount of propylene to the reactor before admission of the methyl halide feed. The compounds trapped in the used catalysts was identified by the method introduced by Guisnet et al. [56,57]. In the catalyst being activated by propylene addition and contacting with methyl chloride for 1 h at 350 °C, the material retained inside the catalyst cages was dominated by methylbenzene isomers. At 450 °C, methyl-substituted naphthalenes were dominant, and higher polyaromatic compounds, such as phenanthrene and pyrene, were detected in appreciable amounts. This implied that the

conversion of methyl chloride and methyl bromide to olefins over SAPO-34 bears a strong resemblance to the more widely studied methanol to olefins reaction [54,55]. Co-feeding of CH₂Cl₂ with CH₃Cl led to rapid catalyst deactivation. Mechanistic studies also showed that CH₂Cl₂ may be incorporated into the methylbenzene reaction intermediates and formed gas phase products via the hydrocarbon pool mechanism. Polymethylbenzyl chloride species was formed by addition of CH₂Cl₂ to the aromatic reaction centers and condensed into heavier compounds and eventually coke species.

4 Aspect of HX as the by-product

For methyl halide conversion to higher hydrocarbons, hydrogen halide, such as HCl and HBr, is released as a by-product. One important question will be the catalyst stability against HCl. In Sun's work [24], he compared the IR spectra of ZSM-5 zeolite with Mg and P modification and exposure to HCl. The HZSM-5 sample exhibited the usual bands at 3745, 3725, and 3605 cm⁻¹, which were assigned to terminal Si(OH), internal Si(OH), and bridge hydroxy group respectively. Mg modification reduced the intensity of Si(OH) group and gave a new absorption of Mg(OH)⁻ ions (3670 cm⁻¹). With further P modification, the intensity of all the hydroxy groups decreased. Contacting the modified ZSM-5 with the dry HCl, no new hydroxy group was produced. In his work, no obvious effect on the catalyst caused by HCl generation could be observed, at least under the reaction conditions.

Lersch and co-workers analyzed the catalysts after chloromethane conversion and found that chlorine was taken up by the deactivated Mg-ZSM-5 catalyst [23]. Some loss of the catalytic active metal component, such as Cu, Fe was also observed after regeneration of these catalysts. They attributed the active metal component loss to the evaporation or sublimation of volatile FeCl₃ or CuCl₂ during the conversion. With these observations, they concluded that for the conversion of chloromethane, solid-state reactions with HCl and vapor phase transport should be considered in metal-exchanged or metal-impregnation zeolites and metal ex-changed zeolites might be destroyed after longtime on stream exposure to the produced HCl, while activation could resume the catalyst.

Olefins and HCl were the main products in methyl chloride transformation using SAPO-34 as catalyst. In Svelle's work, the SAPO-34 catalyst endured several methyl chloride reaction-regeneration cycles at 450 °C. No structural changes in the catalyst were observed by X-ray diffraction after the regeneration tests. This finding indicated that SAPO-34 was a structurally stable catalyst for the conversion of methyl chloride to olefins [41]. Wei and co-workers

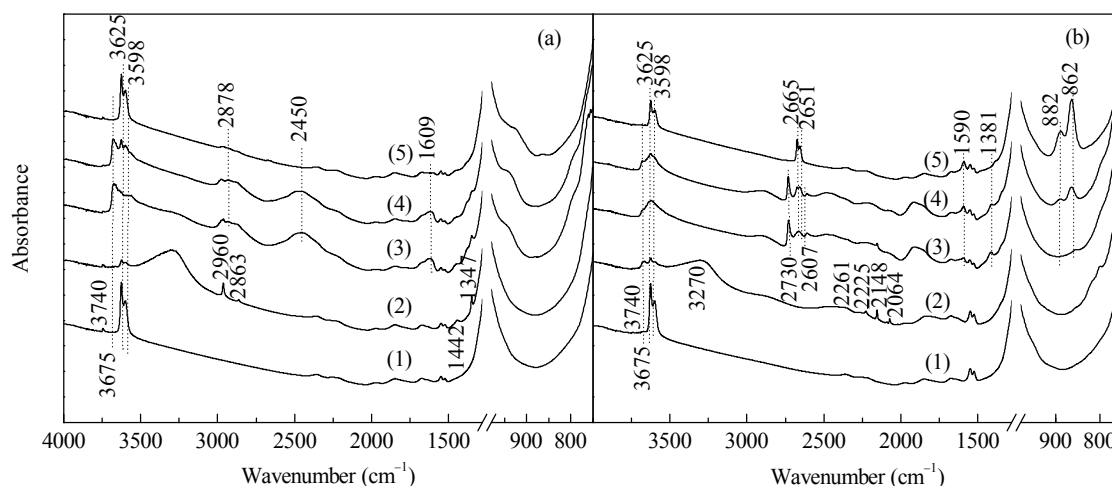


Fig. 8. FT-IR spectra of chloromethane adsorption (15 m/uc) and conversion. (a) CH_3Cl ; (b) CD_3Cl . (1) Activated SAPO-34; (2) Adsorption at RT; (3) Reaction at 450°C for 15 min; (4) Evacuation at RT for 30 min; (5) Evacuation at 150°C for 60 min.

investigated the adsorption and conversion of chloromethane over SAPO-34 catalyst using deuterated CD_3Cl as probe by in situ FT-IR spectroscopy and compared with CH_3Cl [39]. In Fig. 8, the detection of the bridge deuterated hydroxyls $\text{Si}(\text{OD})\text{Al}$ with the absorbances at 2665 and 2651 cm^{-1} indicated the existence of the H and D exchange reaction due to probably the interaction of $\text{Si}(\text{OH})\text{Al}$ and the produced DCl . Very importantly, the reversible and partial breaking of $\text{Al}-\text{O}-\text{P}$ bonds as a result of the produced DCl has been clearly evidenced by the observation of $\text{P}-\text{OD}$ (2730 cm^{-1}) and $\text{P}-\text{OD}-\text{Al}$ (2607 cm^{-1}) species. $\text{Al}-\text{O}-\text{P}$ bonds would be restored upon removal of HCl by evacuation. A very recent work also provided the evidences of the reversibility of the SAPO framework and the crystalline maintenance during the reaction with HCl generation [43].

In gaseous reaction stream, HCl is basically a covalent compound with 18% ionic character and 82% covalent character. Gaseous HCl can interact with catalysts, but does not alter catalyst structure. This also explains the excellent stability of the catalysts. Only at room temperature with humid atmosphere, HCl becomes an acidic compound with strong corrosive character. Production of chlorine-containing compounds or HCl is an old industry. With major production starting in the Industrial Revolution as a chemical reagent, HCl is involved in many industrial processes, such as the large-scale production of vinyl chloride for PVC plastic, pickling of steel, and numerous smaller-scale applications, including regeneration of ion exchangers, household cleaning, leather processing, and swimming pool maintenance. The technique for production and processing of HCl is mature and operable. HCl among the effluents of methylchloride conversion as by-product can be recycled and re-used in the production of methylchloride by chlorination or oxyhydrochlorination reaction with methane. This optimized operation makes methyl chloride trans-

formation to higher hydrocarbons more economical and sustainable.

5 Outlook and conclusion

Natural gas utilization has become a very hot topic because of the energy crisis and great demand of higher hydrocarbons in industry since last century. Especially in recent years, the sharp increase in the price of brut oil calls for the alternative routes for the production of light olefins or gasoline. This gives a great chance for the application of the developed process of natural gas or coal utilization, such as MTO or MTG process, and also accelerate the research of some promising ways for methane transformation to high value-added products. As an alternative way for MTO or MTG process with syngas as the intermediate, the process of natural gas-methyl halide-higher hydrocarbons, with methyl halide as the intermediate, gave a new and promising route for the natural gas utilization. It is of special importance for the area without large-scale methanol supply from abundant syngas precursors and limited access to petroleum. This conversion may also become an alternate for the treatment of the polychlorinated organic compounds (PCOC), which often appear in the industrial hazardous solvent wastes.

As mentioned above in this review, because methyl halide could be produced by monohalogenation of methane under oxidative or non-oxidative condition, for the production of hydrocarbons, a lot of research effort was put on the second step of this process, methyl halide transformation to higher hydrocarbons. In some studies, when the catalytic performances of methyl halide conversion were compared with the result of methanol transformation, it is interesting to find that over the same catalyst, the product distribution maybe same [22]. With this indication, many MTG catalysts

were also employed as the catalyst and promising results have been obtained in the production of hydrocarbons in gasoline range from methyl halides [22–24]. For light olefins production, compared with intense work on Methanol-to-Olefins, the publications for methyl halides conversion to light olefins were relatively limited before 2005. Only Sun and Noronha gave the result of chloromethane conversion on P, Mg or Zn modified ZSM-5 with dominant light olefins production [24,25]. The application of SAPO molecular sieves made the light olefins production from the conversion of methyl halide a very potential way. Chloromethane could be very selectively transferred to light olefins, especially ethylene and propylene, under a mild condition over SAPO-34 catalyst [33,38,41–43]. This work extends the catalyst family for chloromethane transformation and also finds new utilization of SAPO-34, a very excellent MTO catalyst [46].

Some mechanisms for methyl halides conversion to higher hydrocarbons were proposed based on different catalysts. Early studies suggested that methyl halide conversion over zeolite catalysts started from a framework-bound methoxy species and the key step of C–C bond formation was related with a carbene species [28–30], while the later studies of methyl chloride conversion over SAPO-34 presented that the conversion went through an induction period in which cyclic organic reaction center formed and the C–C bond formation from C₁-reactants follow an indirect reaction route [33,41]. Hydrocarbon pool mechanism which has been proposed for methanol conversion was employed in the explanation of methyl halide conversion to hydrocarbons. The similarity in reaction mechanism of C–C bond construction from C₁ reactants, methyl halide and methanol, has been proved.

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