Catalysis Letters 33 (1995) 75–90

An infrared spectroscopic study of the mechanism of chloromethane conversion to higher hydrocarbons on HZSM5 catalyst

Xin-Rui Xia, Ying-Li Bi, Tong-Hao Wu and Kai-Ji Zhen [1]

Department of Chemistry, Jilin University, Changchun 130023, PR China

Received 25 January 1995; accepted 10 April 1995

Investigation of the reaction mechanism of chloromethane on ZSM5 is a new topic. In this work an in situ FTIR technique was employed to study the conversion processes of chloromethane, the active sites on HZSM5, and the desorption state of surface species. The catalytic conversion of chloromethane to higher hydrocarbons was also studied. It is demonstrated that chloromethane can be reversibly adsorbed on acidic sites of HZSM5 at room temperature. At 100°C chloromethane is irreversibly and dissociatively adsorbed on the strong acidic sites of HZSM5, on which surface methoxyl is formed as proved by infrared characteristic C–H stretchings of $-CH_3$ at 2960 and 2870 cm^{-1}. Alkoxyls are produced and adsorbed on the catalyst surface as characterized by the infrared absorption bands of $-CH_2-$ groups at 1460 and 2930 cm^{-1}. At 100°C the adsorbed methoxyl and alkoxyls are the main surface species, and a small amount of aromatics might exist as detected by a characteristic absorption band at 1510 cm^{-1}. Between 100 and 200°C the adsorbed surface methoxyl and alkoxyls are converted to aromatics, and the occupied OH groups partially appear. At temperature higher than 300°C the adsorbed aromatics are thermally desorbed into the gas phase. Aromatics and alkanes are the main products in catalytic conversion. These results reveal that the formation of aromatics from methoxyl and alkoxyls is easier than the desorption of aromatics from HZSM5 catalyst. An alkoxyl mechanism is proposed for the conversion of chloromethane on HZSM5 based upon the experimental results and the three assumptions: (a) The primary C–C bond is formed from surface methoxyl groups via the methoxyl group polarization and C–H bond weakening. (b) The adsorbed alkoxyls are converted to aromatics via hydrogen transfer and bond rearrangement similar to the conventional carbenium ion mechanism for the aromatization of olefins and alkanes on HZSM5. The hydrogen atoms from the aromatization stimulate the desorption of alkoxyls to alkanes. (c) At temperature higher than 300°C surface reactions and desorption of adsorbed species take place simultaneously, determining the product distribution in the catalytic conversion.

Keywords: infrared spectroscopy; chloromethane; HZSM5 catalyst

1. Introduction

The large amount of natural gas (mainly methane) has led to extensive research

---

[1] To whom correspondence should be addressed.

programs [1–3]. It has been demonstrated [4–7] that methane can be catalytically chlorinated or oxychlorinated to chloromethane, which can be converted into higher hydrocarbons over HZSM5 catalyst. The methane conversion processes via chloromethane show several advantages: low energy input, high methane conversion, high hydrocarbon yield and moderate reaction temperature (300–500°C). The conversion of chloromethane to higher hydrocarbons on HZSM5 gives a similar product distribution as the conversion of methanol on HZSM5. It was claimed that a similar reaction pathway on the catalyst surface would be followed in these two cases [1,6].

The conversion of methanol to higher hydrocarbons has been extensively studied for searching an alternative way to obtain high octane gasoline from coal or natural gas rather than from petroleum [8–12]. It has been demonstrated that formation of dimethyl ether intermediate is the first step for methanol conversion on HZSM5 [8]. Concerning the C–C bond formation from C_1 fragments three types of mechanisms have been proposed, (a) carbene mechanisms [9,10], i.e., the C–C bond is formed via carbene ($:CH_2$) intermediates, (b) cation mechanisms [11], i.e., the C–C bond is formed via cation intermediates ($-CH_3$) and (c) methyloxonium ion mechanism [12,13], i.e. the C–C bond is formed from trimethyloxonium ions $(CH_3)_3O^+$ or similar methyloxonium species. Among the three mechanisms the carbene mechanism has been widely accepted because of its consistency with experimental evidence [8–10]. The methyloxonium ion mechanism has also been accepted because the first step of the methanol is via dimethyl ether intermediates [8,12,13]. However, the true mechanism of the initial C–C bond formation from methanol is an unresolved question due to insufficiency of direct experimental evidence [8–13].

The conversion of methane to higher hydrocarbons via chloromethane has several advantages over other routes for chemical utilization of the abundant natural gas. But seldom fundamental works have been reported on this process. The reaction mechanism of chloromethane on HZSM5 remains unknown except for its similarity with the conversion of methanol inferred from the product distribution in these two cases [1,6]. The first step of the conversion of chloromethane is not via the dimethyl ether intermediates. Thus the methyloxonium ion mechanism can be ruled out. The presence of CHl in the reaction system makes it impossible for the carbene mechanism to be accepted, for which abstraction of a proton from the methyl group by basic sites is essential [8–10].

2. Experimental

NaZSM5 zeolite was synthesized by the inorganic ammonia method using SiO_2/Al_2O_3 with a ratio of 38. The NaZSM5 powder was calcined in air at 500°C. The ion exchange of the NaZSM5 with 1.5 N HCl solution under stirring at 80–90°C was repeated four times. The sample was washed with deionized water until no chloride ions were detected anymore, then dried at 120°C, calcined in air at 500°C to obtain the acidic HZSM5. A HZSM5 wafer of about 10 mg/cm^2 was prepared for the infrared experiments. The HZSM5 catalyst was pelletized and sieved to 20–40 mesh for each run.

The infrared spectra were recorded at ambient temperature on a Nicolet Fourier transform infrared spectrometer. A wavenumber range between 400 and 4000 cm^{-1} was scanned with a resolution of 4 cm^{-1}. Each spectrum was obtained with 200 scans. A vacuum system was equipped for in situ adsorption and pretreatment. Chloromethane was introduced under a certain vacuum. It was purified with 5A zeolite, and degassed by repeatedly freezing, pumping, and thawing.

Two adsorption procedures were followed. Procedure I was the adsorption of chloromethane at different temperatures. (a) The HZSM5 wafer was loaded in the cell and heated in flowing air to 450°C, then pumped to 1×10^{-4} Torr. After the in situ pretreatment the cell was sealed and cooled to ambient temperature for recording the infrared spectrum of the activated HZSM5. (b) The HZSM5 wafer was heated to ambient temperature and pumped to 1×10^{-4} Torr. (c) 100 Torr of chloromethane was introduced into the cell at a given temperature for recording the infrared spectra of species both in the gas phase and in adsorbed state. (d) The infrared cell was pumped at ambient temperature to 1×10^{-2} or 1×10^{-4} Torr. (e) The wafer was regenerated as described in step (a) for the next run.

Procedure II was designed to observe the changes of the adsorbed surface species with temperature. (a) The HZSM5 wafer was pretreated in the same way as described in procedure I. (b) After pretreatment the HZSM5 wafer was heated to 100°C and pumped to 1×10^{-4} Torr. (c) 100 Torr of chloromethane was introduced into the infrared cell at 100°C. After 10 min of adsorption the infrared cell was pumped at the same temperature to 1×10^{-2} Torr, followed by sealing and cooling to ambient temperature for recording the spectrum. (d) The sample wafer was heated and pumped simultaneously to a given temperature and 1×10^{-2} Torr. Before scanning the HZSM5 wafer was regenerated as step described in (a) for the next run.

The catalytic conversion of chloromethane to higher hydrocarbons was performed in a conventional flow fixed bed reactor with an on-line GC, which was equipped with a Poropak Q column and a FID detector. The product analysis was performed with a temperature programmed method from 50 to 200°C. The reaction conditions were as follows: 0.100 g of HZSM5 catalyst (20–40 mesh), $He/CH_3Cl = 5$, $F_{CH_3Cl} = 10$ ml/min, at reaction temperatures 250–450°C.

3. Results and discussion

3.1. ACTIVE SITES AND ADSORPTION STATES

As shown in fig. 1, d two absorption bands appear at 3720 and 3608 cm^{-1}, which

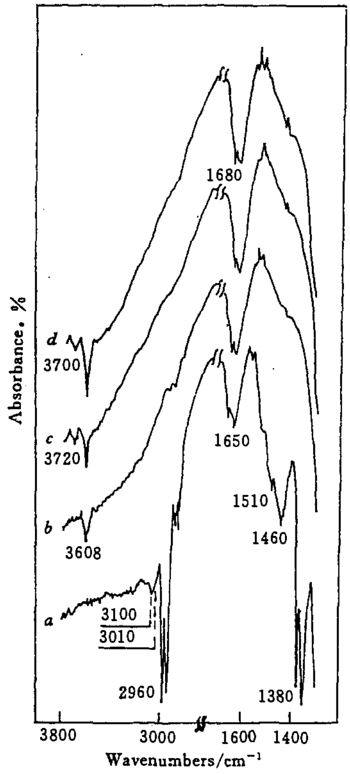


Fig. 1. Reversible adsorption of chloromethane on HZSM5. HZSM5 was pretreated at 450°C and 1×10^{-4} Torr. Adsorption was performed at ambient temperature. 100 Torr of chloromethane was introduced. (a) Spectrum of species both in gas phase and in adsorbed state, (b) pumped to 1×10^{-2} Torr, (c) pumped to 1×10^{-4} Torr, (d) pretreated HZSM5.

are typical OH absorptions of HZSM5 [14]: the absorption at 3720 cm^{-1} is assigned to the stretching of OH groups associated with Si atoms (Si–OH), and the absorption at 3608 cm^{-1} is assigned to the stretching of OH groups bridge-connected between Si and Al atoms (Si–OH–Al). The pyridine adsorption experiment has shown that both kinds of OH groups are Brønsted acidic sites, and that the sites at 3608 cm^{-1} are strong [15].

The infrared spectra of chloromethane species in the gas phase and in the adsorbed state are shown in fig. 1. It is seen that both of the two kinds of OH stretchings disappear at the same time (fig. 1, a), which indicates that chloromethane is adsorbed on both kinds of acidic sites at room temperature. The infrared spectrum of the adsorbed CH_3Cl (fig. 1, a) is similar to that of pure chloromethane in the gas phase and no new absorption bands were detected at room temperature. When the infrared cell was pumped at room temperature to 1×10^{-2} Torr (fig. 1, b), of 1×10^{-4} Torr (fig. 1, c), it was found that all of the chloromethane desorbs and the two OH absorptions appear as in their original state (fig. 1, c, d). No HCl was detected in the desorbed gas meaning that the adsorption of chloromethane on HZSM5 at room temperature is a reversibly undissociative adsorption.

The infrared spectra of the adsorbed chloromethane on HZSM5 at 100°C are shown in fig. 2. Comparing fig. 2, a with fig. 1, a, a new absorption band is seen to appear at 1510 cm^{-1}, and the absorption band at 1460 cm^{-1} increases considerably. When the cell was pumped to 1×10^{-2} Torr (fig. 2, b) or 1×10^{-4} Torr (fig. 2, c), chloromethane was still adsorbed on the surface (fig. 2, b and c). Hydrogen chloride was also detected in the exit gas desorbed. These results indicate that under this condition chloromethane can irreversibly and dissociatively chemisorb on HZSM5.

It is seen that the OH stretching at 3720 cm^{-1} appears after pumping, but the OH stretching at 3608 cm^{-1} does not (fig. 2, b, c). When the wafer was heated to 400°C and pumped to 1×10^{-4} Torr, all of the adsorbed species desorbed. The absorption at 3608 cm^{-1} appears and the infrared spectrum of HZSM5 changes to its original form (fig. 1, d and fig. 2, d). Thus it may be concluded that the irreversibly dissociative adsorption of chloromethane on HZSMT takes place on the acidic sites bridge-connected between Si and Al atoms. This is consistent with the pyridine adsorption experiment revealing that OH groups at 3608 cm^{-1} are strong acidic sites [15].

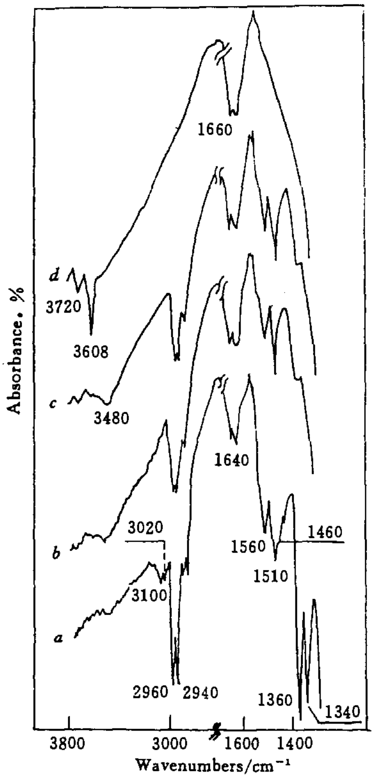


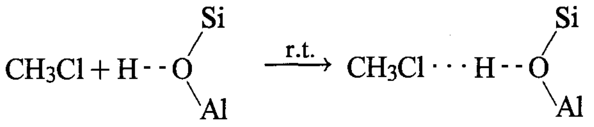
Fig. 2. Irreversible adsorption of chloromethane on HZSM5. The conditions are the same as in fig. 1, except that the adsorbate was introduced at 100°C and for curve (d) the sample was heated to 400°C.

In this work, the standard and literature infrared spectra were used as references (table 1). The absorption bands at 2960 and 2870 cm^{-1} are assigned to the asymmetric and symmetric C–H stretchings of the adsorbed methoxyl (CH_3–O–Z). The absorption bands at 2930 and 1460 cm^{-1} are assigned to the asymmetric stretching and bending of the $-CH_2-$ groups in the adsorbed alkoxyls ($CH_3-(CH_2)_n-CH_2-$O–Z). The absorption band at 1510 cm^{-1} is assigned to the C=C stretching of the adsorbed aromatics.

It is thus concluded that the dissociative chemisorption of chloromethane on HZSM5 at 100°C produces three types of adsorbed surface species, methoxyl, alkoxyls and aromatics. The existence of alkoxyls can be indicated by the infrared absorption band at 1460 cm^{-1}, which is generated by the bonding of $-CH_2-$ groups. In this work methoxyl and alkoxyls are presented as two kinds of surface species that emphasize the dissociative adsorption state of chloromethane and the C–C bond formation process.

From the above mentioned results and discussion, the chemisorption of chloromethane on HZSM5 can be schemed as follows:

surface reactions

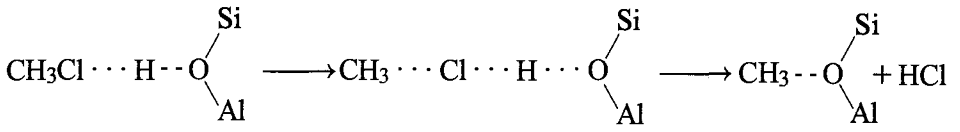


$$CH_3Cl + H\text{--}\overset{\displaystyle Si}{\underset{\displaystyle Al}{O}} \xrightarrow{r.t.} CH_3Cl\cdots H\text{--}\overset{\displaystyle Si}{\underset{\displaystyle Al}{O}} \qquad (1)$$

Table 1
Infrared vibrational frequencies of species

Group		Literature[a]	Experimental	Assignment
$-CH_3$	ν(C–H)	2960as 2870s	2960as 2870s	methoxyl
	δ(C–H)	1450as 1375s	1380s	
$-CH_2-$	ν(C–H)	2925as 2850s	2930as	alkoxyls
	δ(C–H)	1465	1460	
$=CH_2$	ν(C–H)	3020	3020	olefins
	δ(C–H)	1410in 890out		
C=C	ν(C=C)	1650 alkene		
		1496 toluene		
		1520 p-xylene	1510	aromatics
OH	ν(O–H)	3740 Si–OH	3720	HZSM5
		3608 Si–OH–Al	3608	
		3650 alcohol		

[a] Refs. [22,23].



$$\mathrm{CH_3Cl\cdots H{-}{-}O}\genfrac{}{}{0pt}{}{\diagup\mathrm{Si}}{\diagdown\mathrm{Al}} \longrightarrow \mathrm{CH_3\cdots Cl\cdots H\cdots O}\genfrac{}{}{0pt}{}{\diagup\mathrm{Si}}{\diagdown\mathrm{Al}} \longrightarrow \mathrm{CH_3{-}{-}O}\genfrac{}{}{0pt}{}{\diagup\mathrm{Si}}{\diagdown\mathrm{Al}} + \mathrm{HCl} \quad (2)$$

The reactions of the adsorbed species were first examined by the chemisorption of chloromethane on HZSM5 at different temperatures (procedure I). Chloromethane was introduced into the infrared cell and adsorbed on the HZSM5 wafer at a given temperature, then the infrared cell was sealed and cooled to room temperature for recording the infrared spectrum. The infrared spectra of species in the gas phase and in adsorbed state are shown in fig. 3. Comparing fig. 3, a with

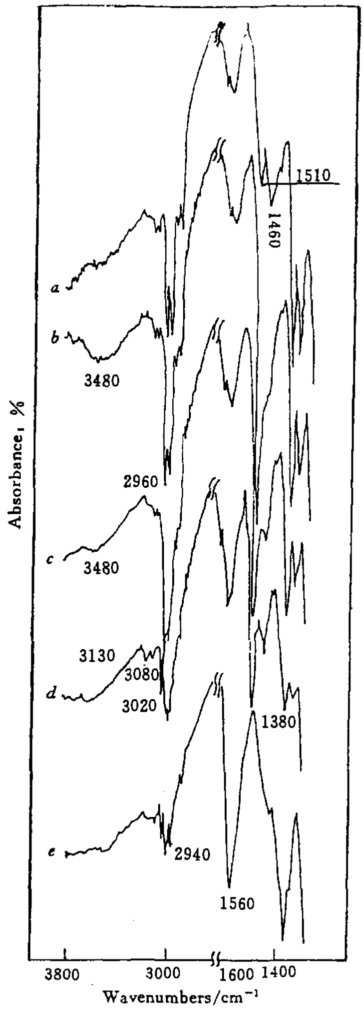


Fig. 3. Infrared spectra of species in both gas phase and adsorbed state at different temperatures: (a) 100°C, (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C.

fig. 1, a it is seen that, at 100°C, a new absorption band appears at 1510 cm^{-1} and the band at 1460 cm^{-1} increases obviously. In fig. 3, b, the absorption band at 1510 cm^{-1} increases significantly. The broad absorption band at 3480 cm^{-1} is also enlarged. The positions of all of the absorption bands are the same as those of species adsorbed at 100°C. The infrared spectrum of the adsorption at 300°C is similar to the spectrum of adsorption at 200°C (fig. 3, b, c). The infrared spectrum of the adsorption at 400°C, however, changes apparently (fig. 3, d). Three new absorption bands at 3130, 3080 and 3020 cm^{-1} appear. The existence of absorption bands between 3100 and 3000 cm^{-1} is usually a criterion of the existence of unsaturated hydrocarbons [14]. The absorption band at 3020 cm^{-1} is assigned to the stretching of =C–H in olefins (table 1). The weak absorption bands at 3130 and 3080 cm^{-1} are attributed to the C–H stretching of aromatics. When the adsorption was performed at 500°C, the HZSM5 wafer became black rapidly and the absorption band at 1510 cm^{-1} disappears. This indicates the formation of coke on the catalyst surface. The absorption bands at 1560 and 1380 cm^{-1} become marked (fig. 3, d) which is suggested to be related with the formation of surface coke [14].

After recording the infrared spectra of species in the gas phase and in adsorbed state the infrared cell was pumped at room temperature to 1×10^{-4} Torr. As shown in fig. 4, the dissociative chemisorption of chloromethane occurs at 100°C (fig. 4, a). At 2960 and 2870 cm^{-1} two absorption bands appear, which are ascribed to the asymmetric and symmetric stretching of C–H bonds in $-CH_3$ groups. The absorption bands at 2930 and 1460 cm^{-1} are ascribed to the C=C stretching of aromatics. Comparing the spectra of the adsorption at 200°C with that of adsorption at 100°C, one can see that, in the former spectrum, the absorption band at 1510 cm^{-1} is very strong, the absorption band of $-CH_2-$ groups at 1460 cm^{-1} decreases significantly. The absorption bands between 2960 and 2870 cm^{-1} also decrease. The absorption bands of $-CH_3$ at 2960 and 1380 cm^{-1} are comparatively stronger than those of $-CH_2-$ groups at 2930 and 1460 cm^{-1}. The broad absorption band at 3480 cm^{-1} becomes broader and larger. These complicated changes of the bands indicate that surface reactions of the adsorbed species occurred when the temperature increased from 100°C to 200°C. It has already been demonstrated that the adsorbed species at 100°C are methoxyl, alkoxyls and aromatics. The infrared spectra clearly indicate that the surface methoxyl and alkoxyls were converted to aromatics when the temperature increased from 100°C to 200°C.

The reactions of adsorbed species are very sensitive to the temperature between 100 and 200°C. This is seen by comparison of the absorption band of $-CH_2-$ groups at 1460 cm^{-1} with that at 1510 cm^{-1} (fig. 5). As the temperature increases the absorption band at 1510 cm^{-1} increases sharply at the expense of the absorption band at 1460 cm^{-1}. At 200°C aromatics seems to be the overwhelming surface species. As pointed out in the previous section, there have already been methoxyl, alkoxyls and aromatics on the catalyst surface at 100°C where the dissociative adsorption of chloromethane began (fig. 2). From the infrared adsorption intensi-

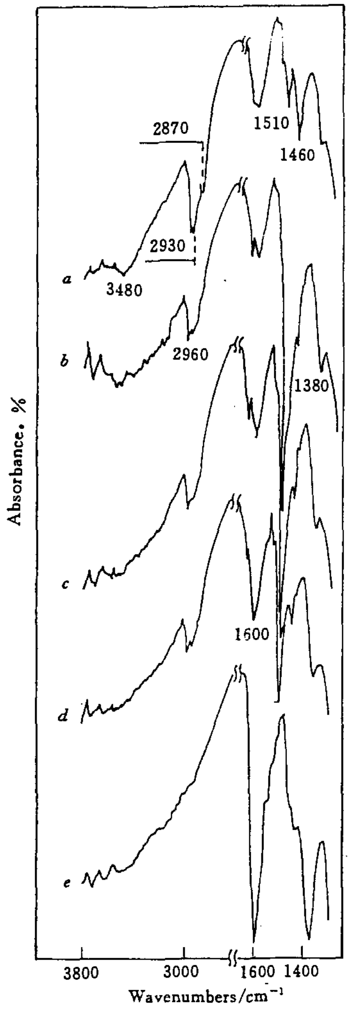


Fig. 4. Infrared spectra of species of adsorbed chloromethane at different temperatures: (a) 100°C, (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C.

ties of the adsorbed species it is known that the amount of aromatics is small; the main adsorbed surface species are methoxyl and alkoxyls. The formation of aromatics at 100°C is assumed to be due to the heterogeneous features of the active sites on zeolite catalysts. The existence of alkoxyls and aromatics reveals that the primary C–C bond has been formed at 100°C, and with the increase in temperature up to 200°C more C–C bonds are formed, the C–C chain lengths grow longer (see the product distribution in table 2) and may probably cyclize to form aromatics.

The infrared spectrum of the adsorption at 300°C is similar to that of the adsorption at 200°C (fig. 4, b, c). The infrared spectrum of the adsorption at 300°C is similar to that of the adsorption at 200°C (fig. 4, b, c). The infrared spectrum of adsorption at 400°C changes considerably. All of the adsorption bands decrease

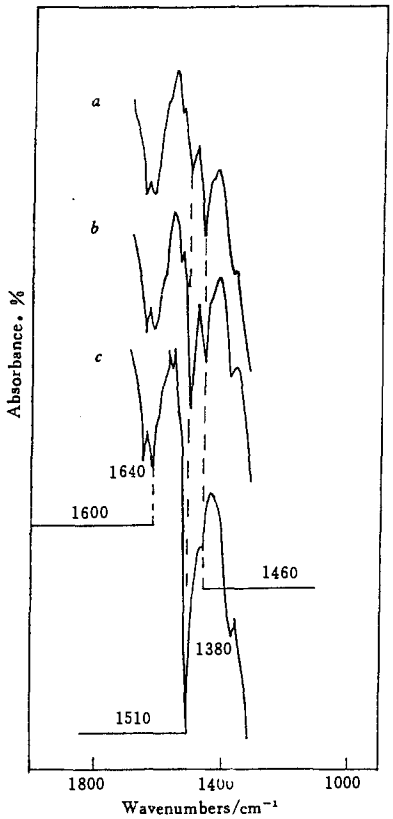


Fig. 5. Infrared spectra of adsorbed species at different temperatures: (a) 100°C, (b) 150°C, (c) 200°C. The sample was pretreated as described in fig. 2.

except the band at 1600 cm^{-1}, which is related with the formation of coke. In the infrared spectrum of adsorption at 500°C, the absorption bands at 2960, 2870 and 1510 cm^{-1} disappear. The bands at 1600 and 1380 cm^{-1} become predominant, indicating that the adsorbed surface species are converted to coke.

Table 2
Chloromethane conversion to higher hydrocarbons on HZSM5 [a]

Temp. (°C)	Conv. CH_3Cl (%)	Selectivity (%)					Yield (%)	
		CH_4	$C_2^=-C_4^=$	C_2-C_4	C_{5+}	A_{6+}	$C_2^=-C_4^=$	A_{6+}
250	3.7	0	60	28.3	11.7	0	2.2	0
300	43	0.3	5.3	34.3	28.1	32	2.3	13.8
350	81	0.9	1.1	38.1	17.4	42.5	0.9	34.4
400	97	1.5	1.8	42.3	10.3	44.1	1.8	42.8
450	99	3.4	3.6	43.8	3.4	45.8	3.6	45.3

[a] 0.100 g HZSM5, He/CH_3Cl = 5, 10 ml/min CH_3Cl at 1 atm.

Comparing the spectra of species in the gas phase and adsorbed state with that of adsorbed species (fig. 3, d, e and fig. 4, d, e), one can see that, when the gas in the cell was pumped out, the infrared absorption of olefins at 3020 cm^{-1} disappeared. This indicates that the detected olefins at the adsorption temperatures higher than 400°C are not adsorbed species, but by-products in the gas phase. This result is important evidence for the reaction mechanism and the existence of the intermediates. A lot of works [8,14,16] claimed the conversion of methanol via olefin chain growth processes, and in some cases olefins were even detected as intermediates characterized by an infrared absorption band at 3020 cm^{-1} [16]. Our experiments [17] show that ethylene and propene are irreversibly adsorbed on HZSM5 at room temperature to form alkoxyls by breaking the double bonds. It is difficult to imagine that olefins can exist on acidic sites of HZSM5 without breaking of the double bonds at higher temperatures. In this work olefins are assumed to be the only by-products desorbed from alkoxyls, e.g., ethylene is desorbed from the surface ethoxyl.

The chloromethane chemisorption on HZSM5 at different temperatures (procedure I) provides important information on the surface reactions of adsorbed species (figs. 3 and 4). In these experiments, however, the surface reactions may involve not only adsorbed species but also reactions in the gas phase. From fig. 6 it can be seen that the spectrum of the adsorbed species (fig. 6, a) is similar to that obtained for adsorption at 100°C in procedure I (fig. 4, a). Three surface species (methoxyl, alkoxyl and aromatics) exist on the catalyst surface. The similarity indicates that the chemisorbed surface species cannot be desorbed by pumping at 100°C and disturbed by the gas phase reactants, which implies that chloromethane participates in further reactions only via the dissociative adsorption.

When the wafer was heated and pumped simultaneously to 200°C and 10^{-2} Torr, the surface adsorbed species undergoes significant changes (fig. 6, b): the absorption band of aromatics at 1510 cm^{-1} becomes predominant, the absorption band of –CH– at 1460 cm^{-1} decreases considerably and those of $-CH_3$ at 2960 and 2870 cm^{-1} are also reduced. At the same time the absorption band of –OH groups at 3608 cm^{-1} emerges. These changes are consistent with those observed in fig. 4, b. Furthermore, it is directly demonstrated that the aromatics are produced from the adsorbed species rather than from reactants in the gas phase. The appearance of part of the –OH groups at 200°C is another proof that surface methoxyl and alkoxyl are combined to form aromatics and the OH groups are exposed.

3.2. CATALYTIC CONVERSION

The results of catalytic conversion of chloromethane on HZSM5 at different temperatures are listed in table 2. When the reaction was carried out at 250°C the conversion of chloromethane was low. The main products were C–C olefins, and no aromatics were detected. When the temperature was increased to 300°C the conversion increased. The selectivity of olefins decreased sharply and a significant

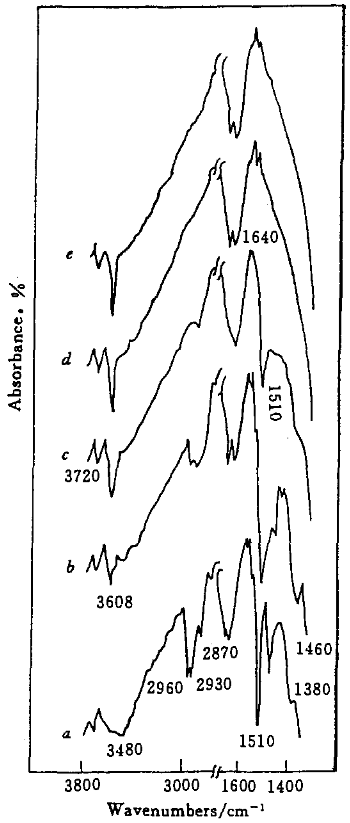


Fig. 6. Infrared spectra of adsorbed species at different temperatures. The sample was pretreated as described in fig. 2. The spectra were obtained after pumping to 1×10^{-2} Torr at the adsorption temperature.

amount of aromatics was produced. These results are consistent with those observed by infrared in the adsorption experiments (fig. 6). At 200°C a large amount of aromatics is formed, but in adsorbed state. Thus no aromatics can be detected in the catalytic reaction. At temperatures higher than 300°C the adsorbed aromatics are thermally desorbed, thus a quantity of aromatics is detected, and the conversion of chloromethane increases considerably.

At temperatures higher than 350°C the conversion of chloromethane is almost complete. The selectivity of aromatics reaches a stable value, the selectivity of higher alkanes (C_{5+}) decreases and that of lower alkanes (C_2–C_4) increases with increasing temperature. In the entire temperature range only a small amount of methane was detected. This implies that it is difficult for methoxyl to be desorbed as methane. The increasing of methane with temperature may be due to a secondary cracking process at higher temperatures. It is also noted that the yields of $C_2^=$–$C_4^=$ olefins are quite low over the entire range of temperature. The increase in the selectivity of $C_2^=$–$C_4^=$ olefins at temperatures higher than 400°C may also be due to secondary cracking [8,14].

3.3. CONVERSION MECHANISM

From the results and discussion mentioned above the following experimental evidence can be used to establish the mechanism of chloromethane conversion on HZSM5:

(a) At room temperature chloromethane is reversibly adsorbed on the acidic sites of HZSM5.

(b) At 100°C chloromethane is irreversibly and dissociatively adsorbed on the strong acidic sites of HZSM5, on which surface methoxyl is formed as proved by infrared characteristic C–H stretchings of $-CH_3$ at 2960 and 2870 cm^{-1} (fig. 2, b).

(c) Alkoxyls are adsorbed on the catalyst surface as characterized by the infrared absorption bands of $-CH_2-$ groups at 1460 and 2930 cm^{-1}. Its adsorption at 100°C leads to the formation of methoxyl and alkoxyls as the main surface species and a small amount of aromatics also exists as detected by a characteristic absorption band at 1510 cm^{-1} (figs. 2 and 4).

(d) At 200°C aromatics become overwhelmingly the adsorbed surface species. At temperatures higher than 300°C the adsorbed aromatics are thermally desorbed into the gas phase. These results reveal that the formation of aromatics from methoxyl and alkoxyls is easier than its desorption from HZSM5 catalyst (figs. 4 and 6).

(e) When surface methoxyl and alkoxyls are converted to aromatics the occupied OH groups are exposed partially (fig. 6).

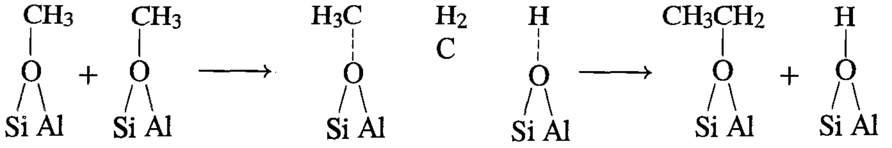
In order to complete the description of the mechanism the following assumptions are made:

(a) The adsorbed alkoxyls are converted to aromatics via hydrogen transfer and bond rearrangement similar to the conventional carbenium ion mechanism for the aromatization of alkanes and olefins on HZSM5 [9,18]. The hydrogen atoms from the aromatization stimulate the desorption of alkoxyls to alkanes.

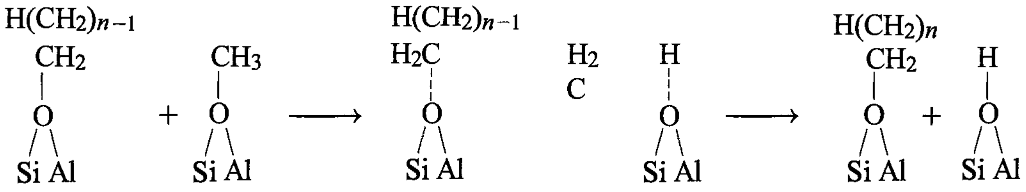
(b) The primary –C–C– bond is formed from surface methoxyl groups via the methoxyl group polarization and –C–C– bond weakening.

(c) At temperatures higher than 300°C surface reactions and desorption of adsorbed species take place simultaneously, which determines the product distribution of the catalytic conversion.

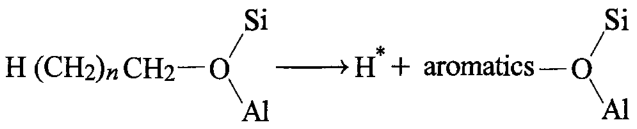
Based upon the experimental results and the three assumptions mentioned above an alkoxyl mechanism can be proposed as follows:



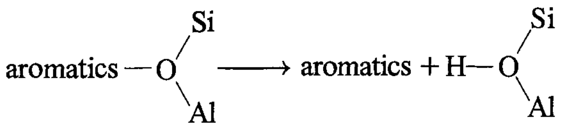
$$\underset{\text{Si Al}}{\overset{CH_3}{\underset{/\backslash}{\overset{|}{O}}}} + \underset{\text{Si Al}}{\overset{CH_3}{\underset{/\backslash}{\overset{|}{O}}}} \longrightarrow \underset{\text{Si Al}}{\overset{H_3C}{\underset{/\backslash}{\overset{|}{O}}}} \quad \overset{H_2}{C} \quad \underset{\text{Si Al}}{\overset{H}{\underset{/\backslash}{\overset{|}{O}}}} \longrightarrow \underset{\text{Si Al}}{\overset{CH_3CH_2}{\underset{/\backslash}{\overset{|}{O}}}} + \underset{\text{Si Al}}{\overset{H}{\underset{/\backslash}{\overset{|}{O}}}} \qquad (3)$$



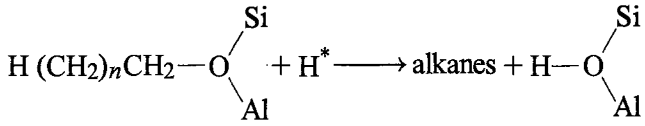
$$\begin{array}{c}\mathrm{H(CH_2)}_{n-1}\\ \mathrm{CH_2}\\ |\\ \mathrm{O}\\ /\ \backslash\\ \mathrm{Si\ Al}\end{array} + \begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{O}\\ /\ \backslash\\ \mathrm{Si\ Al}\end{array} \longrightarrow \begin{array}{c}\mathrm{H(CH_2)}_{n-1}\\ \mathrm{H_2C}\\ \vdots\\ \mathrm{O}\\ /\ \backslash\\ \mathrm{Si\ Al}\end{array} \quad \begin{array}{c}\mathrm{H_2}\\ \mathrm{C}\end{array} \quad \begin{array}{c}\mathrm{H}\\ \vdots\\ \mathrm{O}\\ /\ \backslash\\ \mathrm{Si\ Al}\end{array} \longrightarrow \begin{array}{c}\mathrm{H(CH_2)}_{n}\\ \mathrm{CH_2}\\ |\\ \mathrm{O}\\ /\ \backslash\\ \mathrm{Si\ Al}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{O}\\ /\ \backslash\\ \mathrm{Si\ Al}\end{array} \qquad (4)$$



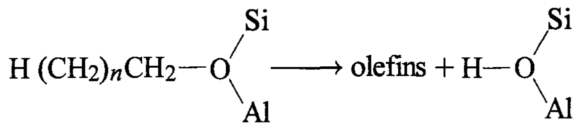
$$\mathrm{H(CH_2)}_n\mathrm{CH_2{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} \longrightarrow \mathrm{H}^* + \text{aromatics}\mathrm{{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} \qquad (5)$$



$$\text{aromatics}\mathrm{{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} \longrightarrow \text{aromatics} + \mathrm{H{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} \qquad (6)$$



$$\mathrm{H(CH_2)}_n\mathrm{CH_2{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} + \mathrm{H}^* \longrightarrow \text{alkanes} + \mathrm{H{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} \qquad (7)$$



$$\mathrm{H(CH_2)}_n\mathrm{CH_2{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} \longrightarrow \text{olefins} + \mathrm{H{-}O}\begin{array}{l}\mathrm{/Si}\\ \\ \mathrm{\backslash Al}\end{array} \qquad (8)$$

In the proposed alkoxyl mechanism, the primary C–C bond is formed from the combination of two methoxyl groups (reaction (3)). In the transient state the methoxyl groups are polarized by the acidic sites and the high static electrical field in the pore of HZSM5 [19], and the C–H bonds in the methoxyl are weakened [20]. The C–C bond is formed via this transient state keeping most features of methoxyl rather than the features of carbene ($:C{-}H_2$) or cation ($-CH_3$) intermediates. This process can be considered as the methylation of one methoxyl with another. Novakova et al. [20,21] found that surface methoxyl groups exhibit appreciable methylation ability, and observed that at above 300°C the surface methoxyl groups, whose C–H bonds are weakened, react to yield a primary C–C bond, and, based upon the observations, pointed out that the reaction of methoxyl with methanol proceeds more readily than reaction between methoxyls.

In this work it is observed that methoxyl and alkoxyls coexist on the catalyst surface even at 100°C. This implies that the alkoxyls have almost the same alkylation activity as the methylation activity of methoxyl groups (reaction (4)). The distribution of methoxyl and alkoxyls and the chain lengths of alkoxyls critically depend on the reaction temperature and reaction time. In literature the chain growth was proposed to proceed via olefins, alcohols or ethers [12–14,24]. However, in our case neither alcohol nor ether was detected.

At higher temperatures the surface alkoxyls may cyclize to form aromatics (reaction (5)). As the chains of the surface alkoxyls grow, the interaction of hydrogen atoms of alkoxyls with zeolite sites becomes stronger, as observed by infrared absorption band at 3840 cm^{-1} (fig. 4).

The surface alkoxyls may undergo a type of carbenium ion like transient state and hydrogen transfer to form aromatics. During the aromatization the hydrogen atoms would stimulate the desorption of alkoxyls to alkanes (reaction (7)). This is consistent with the result that alkanes and aromatics are the main products of the catalytic reaction at higher temperatures (table 2).

By the alkoxyl mechanism olefins are formed by alkoxyl desorption (reaction (8)). This reaction is reversible. Once olefin is adsorbed, it may be converted to alkoxyl, which undergoes further reaction on the catalyst surface. This mechanism provides a constructive clue to the route for enhancing the olefin or aromatics yield. If aromatics are formed, the hydrogen atoms during the H-transfer of aromatization will stimulate the desorption of alkoxyls to alkanes. Aromatics and alkanes are therefore the main products. If the aromatization process of alkoxyls is blocked in some way, then only the desorption of alkoxyls to olefins will be the main process.

It has been demonstrated that the conversion of chloromethane on HZSM5 gives a similar product distribution as methanol conversion on the same catalyst [1,6]. Ione et al. [25] reported that the products of conversion of the substituted methane over zeolites were independent of the substituent, and, for a given catalyst, depended only on the reaction conditions. Our experimental results reached the similar conclusion [17]. Here, a new issue emerges that, whether the same mechanism is followed for the conversion of substituted methane over HZSM5, the product distribution is independent of the substituent.

4. Conclusion

Chloromethane is reversibly adsorbed on the acidic sites of HZSM5 at room temperature. At 100°C chloromethane is irreversibly and dissociatively adsorbed on the strong acidic sites of HZSM5, on which surface methoxyl is formed as proved by infrared characteristic C–H stretchings at 2960 and 2870 cm^{-1}.

Alkoxyls are produced and adsorbed on the catalyst surface, as characterized by the infrared absorption bands of $-CH_2-$ groups at 1460 and 2930 cm^{-1}. In the adsorption at 100°C methoxyl and alkoxyls are the main surface species; a small amount of aromatics also exists as detected by a characteristic absorption band at 1510 cm^{-1}.

Between 100 and 200°C the adsorbed surface methoxyl and alkoxyls are converted to aromatics, which can be characterized by the increase of the infrared absorption band at 1510 cm^{-1}. When surface methoxyl and alkoxyls are converted to aromatics, the occupied OH groups are partially exposed.

At 200°C aromatics become the overwhelmingly adsorbed surface species. At temperatures higher than 300°C the adsorbed aromatics can be thermally desorbed into the gas phase. Aromatics and alkanes are the main products in catalytic conversion. These results reveal that the formation of aromatics from methoxyl and alkoxyls is easier than the desorption of aromatics from HZSM5 catalyst.

An alkoxyl mechanism is proposed for the conversion of chloromethane on HZSM5 based upon the experimental results and the three assumptions: (a) The primary C–C bond is formed from surface methoxyl groups via the methoxyl group polarization and C–H bond weakening. (b) The adsorbed alkoxyls are converted to aromatics via hydrogen transfer and bond rearrangement similar to the conventional carbenium ion mechanism for the aromatization of olefins and alkanes on HZSM5. During the aromatization the hydrogen atoms stimulate the desorption of alkoxyls to alkanes. (c) At temperatures higher than 300°C surface reactions and desorption of adsorbed species take place simultaneously, which determines the product distribution in the catalytic conversion.

References

[1] J.R. Anderson, Appl. Catal. 47 (1989) 177.
[2] J.S. Lee and S.T. Oyama, Catal. Rev. Sci. Eng. 30 (1988) 249.
[3] X.R. Xia, G.X. Xiong, Y.L. Bi, K.J. Zhen and X.X. Guo, J. Nat. Gas Chem., in press.
[4] V.P. Tretyakov and A.N. Osetskii, Kinet. Katal. 23 (1983) 958.
[5] C.E. Taylor and R.P. Noceti, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 2, eds. M.J. Phillips and M. Ternan (Chem. Inst. of Canada, Ottawa, 1988) p. 990.
[6] V.N. Romannikov and K.G. Ione, Kinet. Katal. 23 (1983) 958.
[7] S.A. Butter, A.T. Jurewicz and W.W. Kaeding, US Patent 2 394 107 (1975).
[8] C.D. Chang, Catal. Rev. Sci. Eng. 25 (1983) 1.
[9] P.B. Venuto and P.S.L. Landis, Adv. Catal. 18 (1968) 259.
[10] F.A. Swabb and B.C. Gates, Ind. Eng. Chem. Fundam. 11 (1972) 540.
[11] Y. Ono and T. Mori, J. Chem. Soc. Faraday Trans. I 77 (1981) 2209.
[12] J.P. van den Berg, J.P. Wolthuizen and J.H.C. van Hoff, *Proc. 5th Conf. Zeolites*, Naples 1980, p. 648.
[13] R.H. Nobes, W.R. Rodwell, W.J. Bouma and L. Radom, J. Am. Chem. Soc. 103 (1981) 1913.
[14] W.G. Guo, J. Liang, S.Q. Zhao and R.H. Wang, Cuihua Xuebao 5 (1984) 11.
[15] J.C. Vedrine, A. Auroux, V. Bolis, P. Pejaifve, C. Naccache, P. Wierzchowski, E.G. Derouane, J.B. Nagy, J.-P. Gilson, J.H.C. van Hoff, J.P. van den Berg and J. Wolthuizen, J. Catal. 59 (1979) 248.
[16] Q.N. Dong, Cuihua Xuebao 7 (1986) 22.
[17] X.R. Xia, The mechanism of monosubstituted methane on HZSM5, in preparation.
[18] H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversion* (Academic Press, New York, 1981).
[19] X.H. Guo, X.X. Long, S.X. Xiao and T.L. Chen, Cuihua Xuebao 9 (1988) 396.
[20] J. Novakova, L. Kubelkova and Z. Dolejsek, J. Catal. 97 (1986) 277.
[21] J. Novakova, L. Kubelkova and Z. Dolejsek, J. Mol. Catal. 45 (1988) 365.
[22] G. Mirth and J.A. Lercher, J. Catal. 132 (1991) 244.
[23] L.H. Little, *Infrared Spectra of Adsorbed Species* (Academic Press, London, 1966) p. 1.
[24] B.J. Ahn, J. Armando, G. Perot and M. Guisnet, Compt. Rend. Acad. Sci. C 288 (1979) 245.
[25] K.G. Inoe, V.G. Stepanov and S.E. Shepelev, Khim. Tverd. Topl. 16 (1982) 35.