

Direct catalytic conversion of chloromethane to higher hydrocarbons over a series of ZSM-5 zeolites exchanged with alkali cations

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Abstract

The direct catalytic conversion of chloromethane to higher hydrocarbons at various temperatures over a series of zeolites ZSM-5 exchanged with alkali cations has been studied by means of in situ FTIR and catalytic testing. Hydrocarbons such as aromatics, alkanes and alkenes are formed. A correlation between the acido-basic properties of ZSM-5 zeolites exchanged with alkali cations (Li, Na, K and Cs) and their activity in the direct catalytic conversion of chloromethane has been established. The reaction mechanism has been discussed. The IR observations indicate a production of HCl by elimination from CH₃Cl during the first step of the conversion. A co-operative role of counter ions and the framework oxygen atoms is responsible for the conversion of CH₃Cl in cationic zeolites. Coke formation during the reaction has been investigated by thermal analysis. Significant differences in activity and selectivity can be observed between Li- and NaZSM-5 on one side and K- and CsZSM-5 on the other side. The conversion of chloromethane is quite higher on Li- and NaZSM-5. On the Li and Na forms, the selectivities in C5–C6 are higher. While on K- and CsZSM-5 zeolites the C4 unsaturated products are favoured.

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1. Introduction

Since last petroleum crisis in the 1970s, much research effort has been devoted to convert methane or its derivatives to more valuable hydrocarbons. The very recent sharp increase (in the year 2000) in prices of brut petroleum draws once again the important attention of the world to find new alternatives to petroleum. The main target products of methane conversion are ethylene, propylene and aromatics, for

their extensive use in many chemical processes and high octane gasoline production as well. Because of the low reactivity of methane, the main processes use indirect pathways. Such as conversion to syngas by steam reforming followed by conversion to hydrocarbons over Fischer–Tropsch catalysts. Syngas can also be converted to methanol over Cu/ZnO/Al₂O₃, methanol being then converted to hydrocarbons over HZSM-5 (MTG process) [1–3]. However, despite their great scientific success, these processes showed limited economic interest in the context of conversion of natural gas to hydrocarbons.

In 1985, Olah et al. reported an interesting three-steps route for converting natural gas to higher olefins

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[4]. In this new process, methane is first converted to methyl halide by a selective monohalogenation over supported acid or platinum metal catalysts. In a second step, methyl halide is transformed to methanol by a catalytic hydrolysis reaction and finally to hydrocarbons by MTG process on HZSM-5 catalyst. However, recent studies have shown that this process can be improved by an efficient direct conversion of methyl halide into a mixture of hydrocarbons using zeolites as catalysts [5–10]. The process proposed by Olah can finally be reduced to two steps. Furthermore, this direct conversion should present an interesting alternative for the treatment of the polychlorinated organic compounds (PCOC), which are often the industrial hazardous solvent wastes. At present, these compounds are often decomposed or oxidised to small molecules such as H₂O, CO, CO₂, HCl [11,12]. Therefore, their catalytic conversion to useful hydrocarbons will be an interesting economical and environmental matter.

It has been shown that the direct conversion of chloromethane can be carried out both on acid zeolites like HZSM-5 and HBeta [7–10] and on cationic zeolites such as faujasites X and Y and ZSM-5 exchanged with mono- or divalent cations [5,6,8,9]. CH₃I was also used as mechanistic probe over HZSM-5 and NaZSM-5 and was mainly converted to lower hydrocarbons [13]. The aim of this work is to elucidate the mechanism of this reaction from the initial fragments of CH₃Cl to the formation of the C–C bonds and to study the effect of acido-basicity of zeolites on the activity of catalysts and on the formation of products. A series of zeolites ZSM-5 (Si/Al = 21.0) exchanged with alkali cations (Li, Na, K and Cs) were used.

2. Experimental

2.1. Preparation of catalyst

The starting ZSM-5 zeolite was synthesised with a conventional Na₂O–SiO₂–Al₂O₃–(TPA)₂O–H₂O protocol. The as-synthesised zeolite was calcined at 500 °C under nitrogen flow then under air flow overnight to burn off all the organic template molecules from the porous framework. The various cationic forms were obtained by ion exchange from the calcined zeolite in 1 M chloride solution at room temperature for the Na–, K– and Cs– forms and in

Table 1

Chemical composition of the ZSM-5 after exchange

Zeolite	Chemical composition
LiZSM-5	Li ₄ Al ₄ Si ₉₂ O ₁₉₂
NaZSM-5	Na ₄ Al ₄ Si ₉₂ O ₁₉₂
KZSM-5	Na _{0.4} K _{3.6} Al ₄ Si ₉₂ O ₁₉₂
CsZSM-5	Na _{2.8} Cs _{1.2} Al ₄ Si ₉₂ O ₁₉₂

1 M chloride solution at 80 °C for the Li– form. The exchange degree was verified by atomic absorption spectroscopy. The chemical composition of all the studied zeolites are presented in Table 1. Powder X-ray diffraction measurements were performed to verify that the exchange procedure did not alter the crystallinity of zeolites.

2.2. Direct conversion of chloromethane

2.2.1. In situ FTIR study

Self-supported zeolite wafers (15 mg/cm²) were first calcined in a flow of dry oxygen at 450 °C for 6 h and then in vacuum for 4 h. The spectrum of zeolite phase alone was recorded as a reference using a Perkin-Elmer Fourier Transform Spectrum 2000 Spectrometer. After cooling to room temperature, adsorption of known amounts of CH₃Cl was conducted on zeolite wafers. The conversion of chloromethane was then performed in situ at different reaction temperatures in a range of 100–400 °C during 15 min. After reaction, the samples were cooled to stop the reaction and the IR spectra were then recorded.

2.2.2. Catalytic tests

The catalytic activity and selectivity of zeolite catalysts were evaluated by using a conventional fixed bed microreactor in a flow condition under atmospheric pressure. An amount of 0.100 g of the samples were charged in reactor and calcined in a flow of dry air at 450 °C for 10 h and then the oxidic atmosphere was replaced by He and the temperature of reactor was adjusted to the desired temperature. The CH₃Cl was diluted by He in a molar ratio of 1/4, respectively (WHSV = 0.76 h⁻¹). CH₃Cl and He flows were fixed by mass flow controllers and mixed in a mixer. The products of the conversion were analysed using a Perkin-Elmer 8410 gas phase chromatograph with a FID detector and a HP PLOT Q column.

2.2.3. Coke formation studied by thermal analysis

The coke species formed during reaction were analysed by TG-DSC method. An amount of 30–50 mg of discharged catalyst were loaded in the crucible of the microbalance. The temperature was increased from 20 to 800 °C at a rate of 2 °C/min under dry air flow. The weight loss and calorimetric effect were recorded.

3. Results and discussion

3.1. FTIR study

Only the FTIR study of CH₃Cl performed over NaZSM-5 is reported here. The IR absorbance spectrum of the activated NaZSM-5 zeolite is shown in Fig. 1a. In the 1200–4000 cm⁻¹ range, only a small peak at 3747 cm⁻¹ is observable and corresponds to

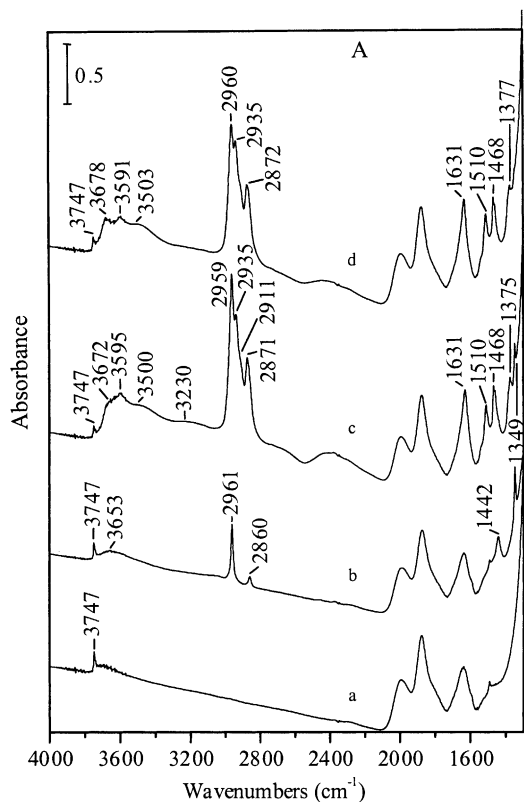


Fig. 1. Adsorption and conversion of CH₃Cl over NaZSM-5, (a) activated NaZSM-5, (b) CH₃Cl at RT, (c) after heating 15 min at 400 °C, (d) after 30 min of desorption at RT.

external silanols, the absence of bridging framework OH groups indicates that the ion exchange is complete.

The introduction of chloromethane at room temperature brings the appearance of four new peaks at 2961, 2860, 1442 and 1349 cm⁻¹ corresponding, respectively to anti-symmetric and symmetric stretchings and bendings of methyl group of CH₃Cl (Fig. 1b). An interaction between CH₃Cl and external silanols is also observed and induces a shift of the silanols to 3653 cm⁻¹.

At room temperature, no conversion of chloromethane is observed. However, with increasing reaction temperature, peaks at 1387, 1468 and 2935 cm⁻¹, assigned to –CH₂– vibrations and at 1631 cm⁻¹, corresponding to the vibrations of –C=C– are observed from 100 °C. After heating for 15 min at 400 °C (Fig. 1c), vibrations characteristic of higher hydrocarbons (–CH₂– stretchings and bendings, C=C stretchings and deformation) are detected. The observation of these vibrations indicates clearly that C–C bond formation occurs and that higher hydrocarbons are produced. Attributions of all the vibration bands observed for the products of conversion are given in Table 2.

It is interesting to observe several broad bands centred at 3230, 3500, 3595 and 3672 cm⁻¹ after reaction at 400 °C. These broad features are usually observed in protonated zeolites in the presence of alkenes, aromatics or chloromethane [14–16]. They are attributed to the accessible hydroxyls shifted to lower wavenumbers because of their interaction with olefins, aromatics or chloroalkanes. The presence of these broad bands after reaction at higher temperature on cationic ZSM-5, which is free of OH groups after pretreatment, indicates the creation of hydroxyls on this zeolite and confirms the formation of olefins or aromatics from the conversion of chloromethane. The hydroxyls on this cationic zeolite are probably generated by the interaction of framework oxygen atoms with HCl as a product of the conversion. This suggests that in the first step of the conversion, a dehydrohalogenation occurs on NaZSM-5 during the dissociation of CH₃Cl. Indeed, an HCl adsorption study over NaY has shown that hydroxyl groups are generated at room temperature by the action of hydrogen chloride molecules on framework oxygen of the zeolites [17]. Furthermore, an other study over cationic faujasites has shown that OH groups are also produced in the presence of *n*-propyl

Table 2

Wavenumbers and assignments of IR peaks for the products observed over NaZSM-5

Wavenumbers (cm ⁻¹)	Assignments	Wavenumbers (cm ⁻¹)	Assignments
2961	$\nu(\text{C-H})_{\text{as}}$ of $-\text{CH}_3$	1468	$\delta(\text{C-H})$ of $-\text{CH}_2-$
2935	$\nu(\text{C-H})_{\text{as}}$ of $-\text{CH}_2-$	1442	$\delta(\text{C-H})_{\text{as}}$ of $-\text{CH}_3$
2871	$\nu(\text{C-H})_{\text{s}}$ of $-\text{CH}_3$	1387	(CH ₂) deformation
1631	$\nu(\text{C=C})$ of alkenes	1377	(CH ₂) deformation
1510	(C-C) of aromatics	1349	$\delta(\text{C-H})_{\text{s}}$ of $-\text{CH}_3$

chloride. The authors assumed that phenomenon was caused by the presence of HCl molecules produced by dehydrohalogenation [18].

The desorption of species adsorbed on NaZSM-5 at room temperature (Fig. 1d) results in a slight decrease of the broad bands in intensity, indicating the removal of a part of the hydrocarbons produced and unreacted chloromethane. However, hydrocarbon peaks are still quite intense, indicating that some products are strongly adsorbed on the framework.

This part of the results reveal that higher hydrocarbons are really formed on NaZSM-5 from CH₃Cl and the production of HCl leads to the formation of hydroxyls in NaZSM-5.

3.2. Catalytic tests

3.2.1. Effect of temperature on the direct conversion of chloromethane

ZSM-5 in Li, Na, K and Cs form have been used. The effect of reaction temperature on the catalytic conversion was first studied. Temperature effects over conversion rate for these four zeolites are shown in Fig. 2. A low activity is observed under 200 °C. At 200 °C, the conversion ranks in the order LiZSM-5 > NaZSM-5 > KZSM-5 ≈ CsZSM-5. At higher temperatures, the conversion rate increases highly for Li and NaZSM-5, slightly for KZSM-5 and remains almost constant for CsZSM-5. At all the temperatures, the same order of activity as for 200 °C is practically observed: LiZSM-5 > NaZSM-5 ≫ KZSM-5 > CsZSM-5. The Li and Na forms show very good conversion rate, but ZSM-5 catalysts in K and Cs forms give lower activity. This is probably due to the large size of these counter ions, weaker Lewis acids, which interact less strongly with the chlorine atom of chlorinated hydrocarbons during the conversion. This interaction should be more efficient with cations hav-

ing higher Lewis acidity. We will discuss the above observations in Section 3.2.2.

3.2.2. Selectivities

The effect of temperature over the selectivities for Li, Na, K and CsZSM-5 zeolites are shown in Fig. 3. Only the variations of the hydrocarbon products are given. No significant change in selectivity of chlorinated compounds with temperature is noted and therefore their selectivity is not displayed in Fig. 3. These compounds are mainly HCl, C₂H₅Cl and C₃H₇Cl, no Cl₂ or dichlorinated hydrocarbon molecules are observed.

As a general tendency, it is observed that in the studied temperature range, C₂–C₆ hydrocarbons such as ethylene, propane, butane isomers, aromatics and HCl are the major products. Heavier hydrocarbons (C₄–C₆) are favoured at lower temperatures, while lighter compounds are in majority from 300 °C. This is due to a further cracking of heavy products formed

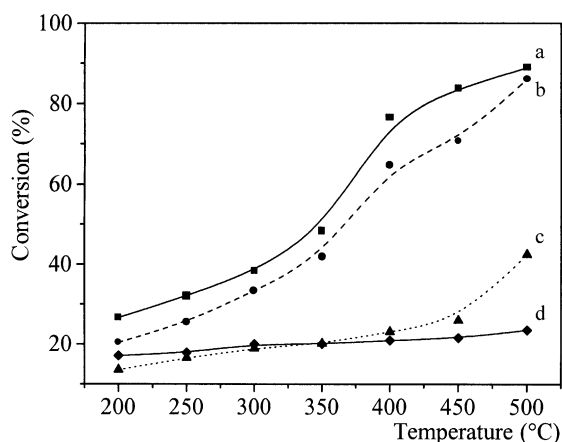


Fig. 2. Conversion of CH₃Cl over cationic ZSM-5, initial activity at various temperatures, (a) LiZSM-5, (b) NaZSM-5, (c) KZSM-5, (d) CsZSM-5.

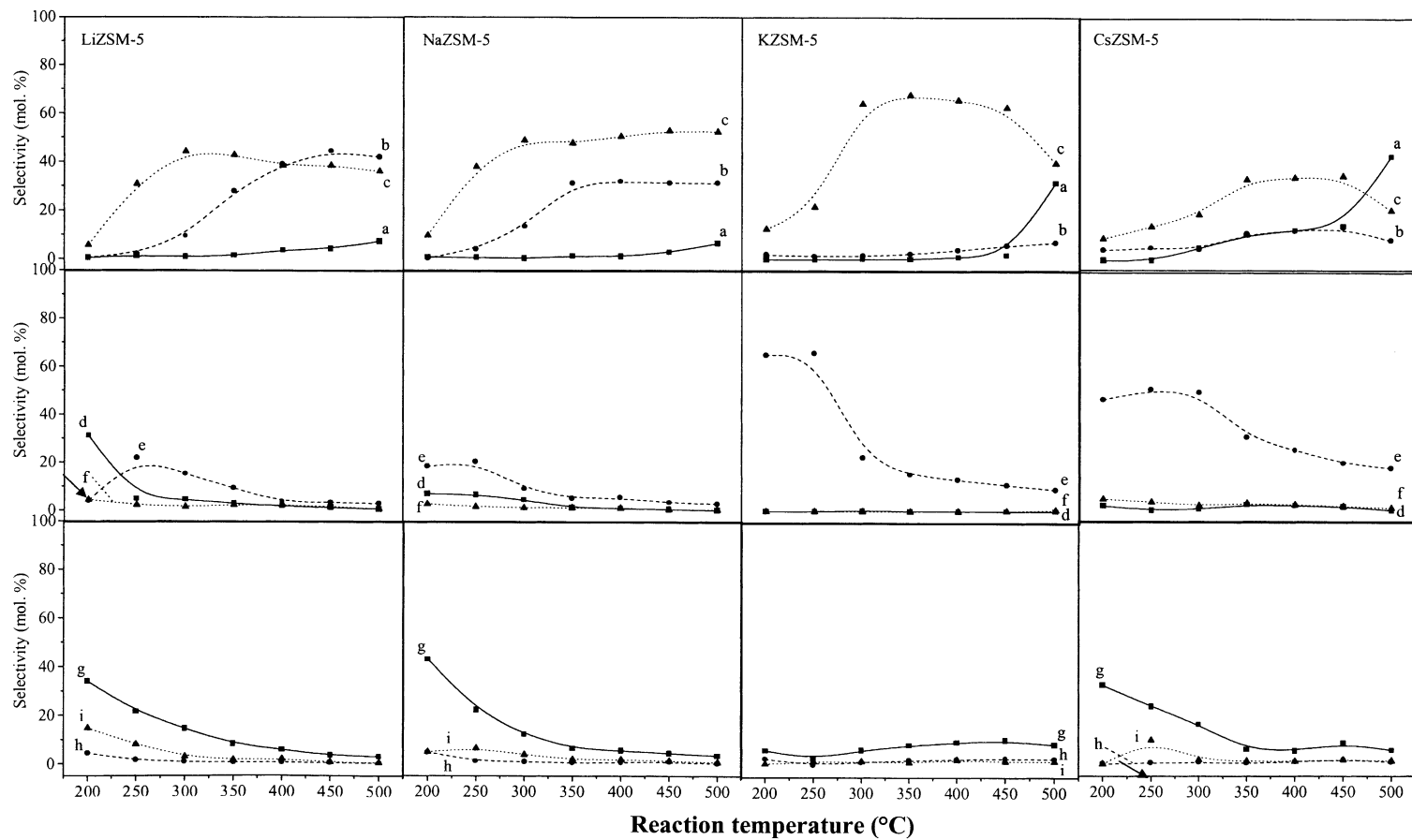


Fig. 3. Product selectivities over the four cationic ZSM-5 at various temperatures, (a) CH₄, (b) C₂H₄, (c) C₃H₈, (d) *i*C₄H₁₀, (e) C₄H₈, (f) *n*C₄H₁₀, (g) C₅, (h) A₆, (i) C₆.

at higher temperatures, the main part of the C4–C6 molecules being cracked back to C1–C3 molecules. No propylene is observed, while ethylene and propane are produced, this is probably because of the higher reactivity of propylene which is rapidly converted to higher hydrocarbons after its formation. Indeed, some studies have shown that propylene oligomerizes quickly at room temperature over acidic zeolites [19].

Over LiZSM-5, a greater selectivity of isobutane in comparison with *n*-butane is observed, this phenomenon is common in many methane conversion or butane reaction processes. It can be easily explained by a carbene or carbonium mechanism for the addition of a C1 intermediate on propylene [3]. The selectivity in isobutane reaches 31% at 200 °C, giving a iC_4H_{10}/nC_4H_{10} ratio of 7/1. This ratio and the selectivity in isobutane decrease with temperature and C1–C3 production increases due to the cracking reaction of heavier products at higher temperatures.

Over all the zeolites, from 400 °C methane selectivity increases quickly with temperature. This undesired methane production can also be observed after several hours at 450 and 500 °C. Indeed, it is known that deactivation caused by coke formation is often linked with an increase of the methane selectivity. The thermal analysis study will show that coke production occurs in the zeolites during the conversion reaction.

It can be observed over the four zeolites, that the selectivity in ethylene reaches a stable value between 300 and 400 °C, which is strongly dependent on the

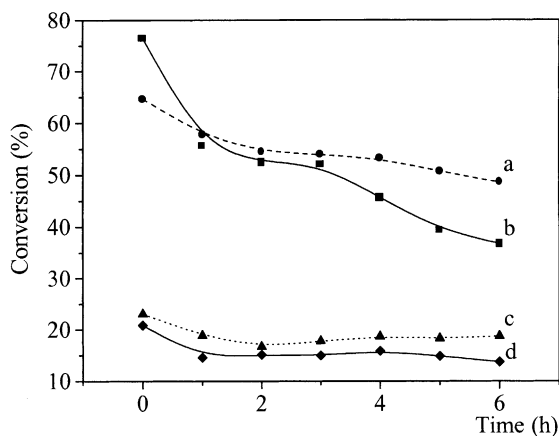


Fig. 4. Aging tests over cationic ZSM-5 at 400 °C; (a) LiZSM-5, (b) NaZSM-5, (c) KZSM-5, (d) CsZSM-5 (WHSV = 0.76 h⁻¹).

cationic type of the zeolite, with temperature. Furthermore, the ethylene selectivity decreases with bigger cation size. While propane selectivity increases with cation size. It is also interesting to emphasise that ethylene production is greatly enhanced with temperature over LiZSM-5, giving a selectivity of 45% at 450 °C.

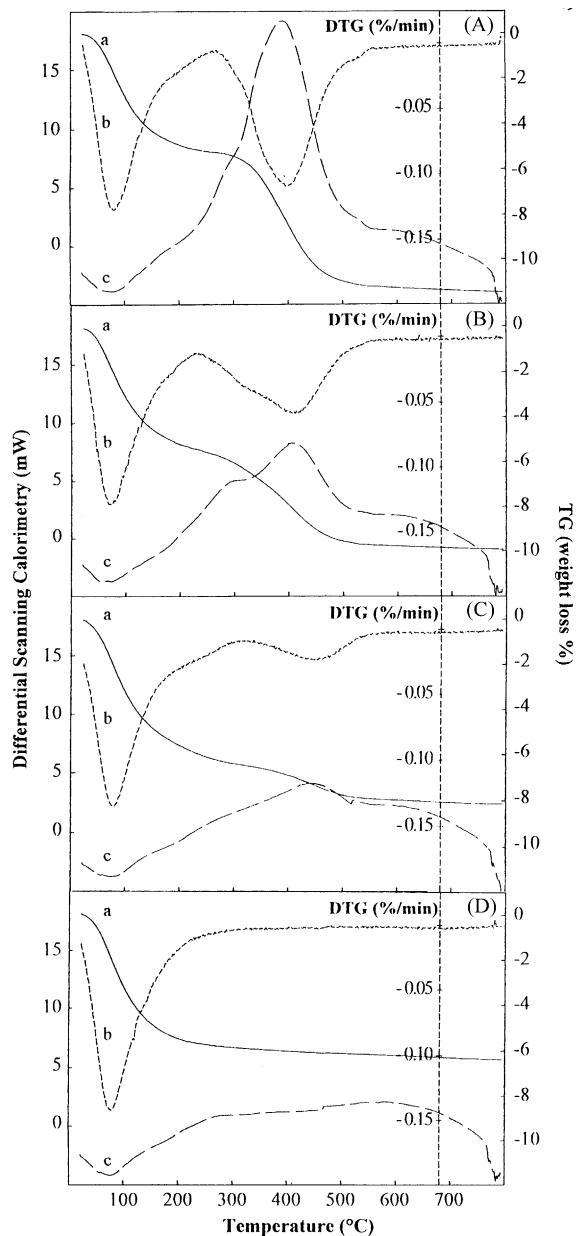


Fig. 5. TG-DSC study of coke formation over aged cationic ZSM-5.

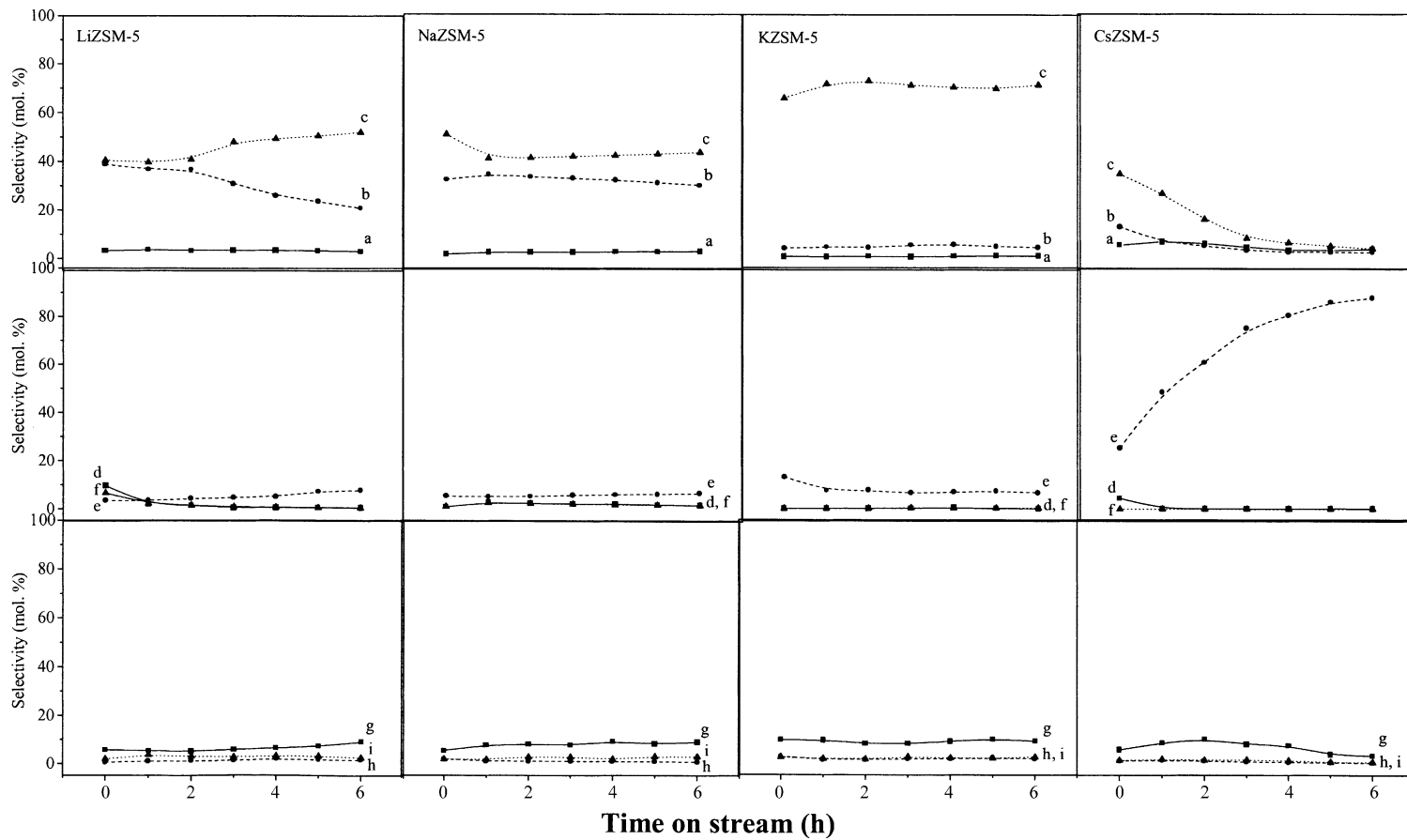


Fig. 6. Time variations of product selectivities over cationic ZSM-5 at 400 °C, (a) CH₄, (b) C₂H₄, (c) C₃H₈, (d) iC₄H₁₀, (e) C₄H₈, (f) nC₄H₁₀, (g) C₅, (h) A₆, (i) C₆.

Significant differences can be observed between Li- and NaZSM-5 on one side and K- and CsZSM-5 on the other side. On the Li and Na forms, the selectivities in C5–C6 are quite higher than those for K- and CsZSM-5. While on these last zeolites the C4 unsaturated products are favoured. Furthermore, the selectivities in C4 saturated isomers diminish with cation size and almost disappear over K and CsZSM-5. This is probably because of the greater activity of Li- and NaZSM-5 zeolites in which C4 unsaturated compounds, which strongly seem to be the main intermediate between C3 and C5 products, are rapidly saturated or converted to heavier products, while these C4 products have a longer lifetime and may

diffuse out of the catalyst on the less reactive K- and CsZSM-5.

It should also be noted that for K and CsZSM-5, the C₄H₈ and C5–C6 selectivities decrease less rapidly than those over Li and NaZSM-5. Furthermore, these compounds reach a stable value of selectivity at higher temperatures. This is probably due to a lower reactivity which induce a lower cracking effect. However, the methane production at 450 and 500 °C increases with the cation size, giving more this undesired product over K and CsZSM-5.

Concerning aromatics, the selectivity results also show that these compounds are cation size dependent. Indeed, their selectivity decreases from LiZSM-5 to

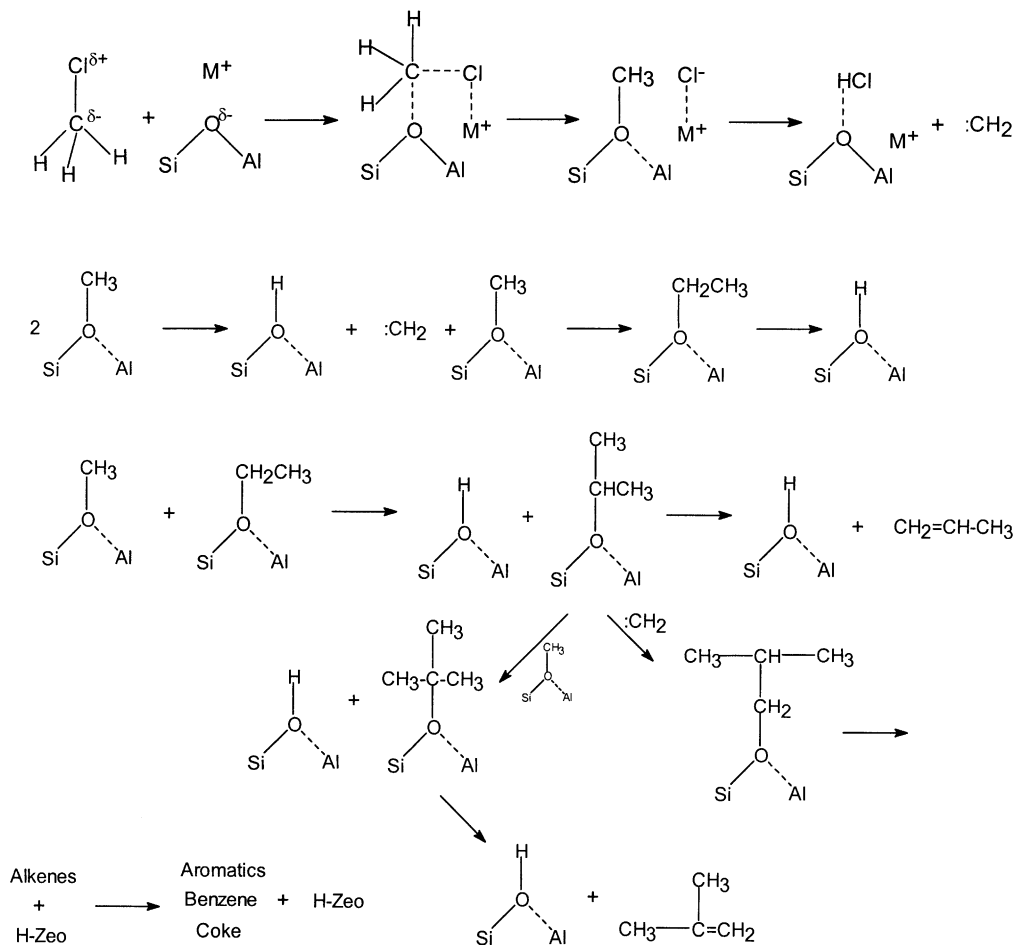


Fig. 7. Proposed mechanism for chloromethane dissociation over a cationic zeolite.

CsZSM-5, probably because a higher Lewis acid is more efficient for the amortisation reaction.

3.2.3. Aging of catalysts

The effect of time on stream over conversion rates was carried out during 6 h. Results for the four studied zeolites are shown in Fig. 4. The aging tests show that the Li and NaZSM-5 deactivate significantly, while the KZSM-5 and CsZSM-5 zeolites have only very slight deactivation because of the low activity of these zeolites which induce slower coke formation. This is in agreement with the order of activity obtained for these zeolites, indicating that a higher activity induces a more important coke formation.

This assumption is confirmed by the TG-DSC analysis of discharged catalysts after 6 h reaction (Fig. 5). These analyses show three weight loss regions (TG curve) in 25–200, 230–400 and 300–550 °C under dry air flow condition with a programmed temperature increase. The first is an endothermic loss which can be easily attributed to water desorption in the discharged catalysts and the two others are exothermic and correspond to the combustion of coke species deposited in the pores of zeolites. It is well known that ZSM-5 zeolite contains medium pores without large cavities, the accumulation of cokes in the pores is therefore not favoured. However, at least two different coke species are still formed.

It is interesting to observe that the weight loss due to cokes decrease from LiZSM-5 to CsZSM-5. This shows that more coke is formed over the zeolites with higher Lewis acidity. As it is well known that the Lewis acid sites such as counter ions favour the coke formation [20,21], we assume that the alkali cations of the studied ZSM-5 must be the main site of production of coke. As a consequence, these active sites will be blocked by the formed coke and will be no longer accessible for methyl chloride molecules causing a decrease of conversion rate. Furthermore, the coke formed has a pore blocking effect which handicaps diffusion of reactant to active sites as well as products outing of the catalyst.

Selectivity charts versus time on stream are shown in Fig. 6. Except for CsZSM-5, no significant change in selectivity is observable with time on stream. The main changes occur between initial injection and 1 h, indicating that the catalyst reaches a steady state after a short reaction time.

Over LiZSM-5, the decrease of C₂H₄ and increase of C₃H₈ in selectivity must be linked with deactivation and coke formation. Accumulation of HCl molecules should also be a reason of these variations as they should favour the ethylene to propane conversion. Over CsZSM-5, an accumulation of new acid sites due to the presence of HCl molecules should have a greater catalytic role than the weak Lewis acidic cesium counter ions and then influences progressively some product selectivities. That is why a more important variation of selectivities is observable over CsZSM-5 than for the other cationic ZSM-5.

4. Discussion

The above results indicate that a high Lewis acidity of the counter ion is active for the conversion of chloromethane.

Over NaZSM-5 the FTIR results show that chloromethane can interact by its chlorine atom with the silanol groups. Previous works have shown that at room temperature, chloromethane is reversibly adsorbed on HZSM-5. But from 100 °C, the dissociative and irreversible adsorption start [7]. Methyl chloride should then dissociate with the help of oxygen atoms of the framework, acting as basic sites, and the participation of the counter ion giving methoxy species (Fig. 7). This is confirmed by the catalytic test results. Indeed, both Li and NaZSM-5 show good conversion rate, but the K and CsZSM-5 forms (which are more basic since the oxygen atoms of the framework are more negatively charged) give lower activity. This is probably due to the size and Lewis acidity of these counter ions, which interact weakly with the chlorine atom during the conversion. This interaction should be more efficient with lithium and sodium. The order of activity which has been established by our measurements, LiZSM-5 > NaZSM-5 > KZSM-5 > CsZSM-5, indicates that the counter ion must participate in the dissociation of the methyl chloride molecule, which is the first step of the process. The chloromethane molecules are dissociated by interacting both with cation, by its chlorine atom, and oxygens of the framework. The FTIR results over NaZSM-5 indicate that the chloromethane conversion should occur via a dehydrohalgenation as first

step. This is clearly demonstrated by the presence of the new OH bands observed.

Then the first C–C bond formation should occur via a carbene transfer between neighbouring methoxy group (Fig. 7). This mechanism is commonly observed in many catalytic and organic reaction processes. The C–C link is formed by the carbene insertion in C–H bond of a methoxy group. From this first insertion, other insertions can happen and increase the chain length. But other type of reaction can also occur. Indeed, as alkenes may be present, they can react with carbonium intermediate or proton. It is observed that different isomers such as normal or isobutane are formed. Assuming that these C4 hydrocarbons are produced by the addition of a carbene or carbonium intermediate over propylene, the iso compound is favoured, because in both cases this reaction arise from tertiary butyl cation as an intermediate [3]. For pentane and hexane compounds, the number of isomers increases, they are synthesised via a similar mechanism as for C3–C4 reaction. Because these isomers are quite difficult to separate under conditions used, the selectivity results are presented as “C5” or “C6” on the charts. Concerning aromatics, they can be synthesised by cyclisation of alkoxy groups adsorbed on the zeolite. During this process, H-transfer happens, which may also favour the formation of alkanes. Indeed, if aromatic compounds are observed, alkanes, rather than olefins, are also produced [7].

All the selectivity results over the cationic zeolites are more or less directly dependent of the cation activity toward the various hydrocarbons. The decrease of the ethylene selectivity over zeolites with bigger cation size indicates that the main part of this C₂H₄ should be produced by cracking of C5–C6 compounds. This indirect production is added to the direct ethylene synthesis, which is commonly admitted to be the first compound produced from methane derivatives conversion. The weaker Lewis acids, the weaker cracking, this is in agreement with selectivity results for the cationic zeolites.

The production of C₃H₈ over the cationic zeolites, over which one could assume that C₃H₆ would rather be observed, can be explained by the reaction of C₃H₆ with protons produced by the dehydrohalogenation of CH₃Cl to carbene (Fig. 7). This reaction could occur quicker than that of the chain growth, for which an active cation is necessary at least for CH₃Cl

dissociation, over the weaker Lewis acid zeolites. The different result for CsZSM-5 can be explained by greater selectivities of CH₄ and C₄H₈ which are even more favoured than propane.

For all the zeolites, ethyl chloride is found. It comes from a reaction between ethylene, one of the main product, and hydrogen chloride, produced by elimination from CH₃Cl, or by a carbene insertion in C–H bond of a CH₃Cl molecule.

The aging test results show clearly that Li- and NaZSM-5 catalysts deactivate quickly while K- and CsZSM-5 catalysts decrease in conversion only weakly. These results are quite in agreement with thermal analysis study on the coke formation for which the amount of coke formed decreases from Li, Na, K to CsZSM-5. Due to the larger size of K and Cs, there is less available space in the framework for the accumulation of coke and therefore less coke formation.

One may think that the deactivation of catalysts can also be caused by dealumination of zeolites since an important amount of HCl is formed by this reaction. However, we believe this is less probable, even though HCl can be formed, since the reaction is carried out in a range of 200–500 °C in a gas flow system without humidity. Gaseous HCl is a covalent compound with 19% of ionicity. It can not extract Al atoms from the framework. Therefore, this possibility can be eliminated and the deactivation is mainly due to the coke formation. This suggestion is confirmed by the TG-DSC study.

5. Conclusion

The present work shows that cationic zeolites could be the very efficient catalysts for the direct conversion of chloromethane to higher hydrocarbons such as ethylene, propane, butane isomers and aromatics. The chlorine atom is removed from the reactant, in the same time, hydrogen chloride and small quantities of ethyl chloride are formed, giving mainly unchlorinated hydrocarbons. Zeolites exchanged with Na or Li cations are more active. The initial catalytic activity ranks in the order: LiZSM-5 > NaZSM-5 ≫ KZSM-5 > CsZSM-5. Catalyst aging tests have shown that the most active zeolites are deactivated more quickly. This is confirmed by the TG-DSC coke formation study which shows a straight correlation

between cation size and the quantity of coke formed. The counter ions must be the active sites for the production of coke. However, the selectivity of the products seems not to be affected, at least not significantly, by aging, while reaction temperature and counter ion has an important effect on selectivity. The acido-basic and structural properties of zeolites influence also strongly the conversion and aging of catalysts.

A co-operative role of counter ions and the framework oxygen atoms is responsible for the conversion of chloromethane in cationic zeolites. A stronger Lewis acidity of the counter ion enhance the activity. On the basis of the above results and combining with our previous IR studies [8], a reaction mechanism implying an initial fragment of chloromethane by a dehydrohalogenation is proposed. In this mechanism, the CH_3Cl molecules interact with the cation of the zeolite by the chlorine atom and then the C–Cl bond is dissociated because of another interaction with the oxygens of the framework.

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