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Conversion of chloromethane to light olefins catalyzed by ZSM-5 zeolites

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Abstract

The conversion of chloromethane to light olefins, like ethene and propene, was studied over ZSM-5 catalysts at 698 K. For HZSM-5, the selectivity to olefins increased for higher Si/Al ratio and was interpreted in terms of reducing hydrogen transfer, as the sites become more isolated. The exchange of Zn^{2+} cation increased the activity and selectivity to light olefins. Theoretical calculations using a MT_6 cluster (T = Si or Al and M is an alkaline cation) showed that the activation energy for the formation of an adsorbed methoxide from chloromethane increases in the alkaline metal series, with Li^+ showing the lowest and Cs^+ the higher barrier. The calculations also indicated that the metal–chloride interaction plays an important role in the reaction.

Keywords: Zeolites; Chloromethane; Olefin; ZSM-5; GTL; DFT

1. Introduction

The search for industrial processes for replacing naphtha as raw material to produce petrochemicals is a major challenge in chemistry. Traditionally, light olefins, ethene and propene, are produced by the steam cracking of the naphtha [1]. With the increasing price of oil and uncertainty in continuous supply during the 21st century, other sources for producing light olefins are desired. Hence, natural gas appears as a promising raw material, because the world gas reserves exceed the oil reserves. In addition the gas reserves are spread all over the world, being less prone to political conflicts in a specific place.

Some progress on this subject has been achieved with the development of the methanol to olefins (MTO) process [2]. This reaction is catalyzed by SAPO-34 molecular sieve and produces ethene and propene as main products. However, methanol is produced from synthesis gas, whose formation from natural gas is energetically demanding, increasing processing costs. Therefore, the development of alternative processes from natural gas, skipping syn gas formation, is desired.

Methane is a high stable molecule. Many acid systems and oxidant reagents are inert toward methane, which makes functionalization and activation of its C–H bond a difficult task. On the other hand, halogenation of methane is a well-known reaction, which proceeds through free radicals, or can even be achieved with use of a proper catalyst [3]. Chlorination is exothermic by 101 kJ/mol, while bromination releases only 25 kJ/mol. Both reactions are performed in industrial scale to produce the halomethane derivatives.

The use of chloromethane as substitute for methanol in the methanol to gasoline (MTG) process has been claimed in some patents [4,5]. Early work of Ione and collaborators reported that chloromethane could be converted to hydrocarbons over HSZ zeolite [6]. In more recent publications [7–11] on the chloromethane conversion to hydrocarbons, metal-exchanged zeolites have been investigated. Jaumain and Su reported a study of chloromethane conversion to higher hydrocarbons over a series of alkali-exchanged ZSM-5 zeolites [12]. The results indicated that activity decreases from Li^+ to Cs^+. The authors proposed an interaction of the chlorine atom with the alkaline cation metal as the first step

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Table 1
Chemical and textural analysis of the HZSM-5 zeolites

Parameter	HZSM-5 (28)	HZSM-5 (82)
Surface area (m^2/g)	374	413
Micropore volume (ml/g)	0.1311	0.098
Si/Al ratio[a]	28	82
Na_2O[a] (%)	<0.05	<0.04

[a] Measured by X-ray fluorescence.

of the reaction, but did not proposed an explanation for the activity order.

We wish to present here results of the conversion of chloromethane over HZSM-5 and Zn-exchanged ZSM-5 zeolites, focusing on the selectivity toward ethene and propene. In addition, we present theoretical calculations for the interaction of chloromethane with alkali-exchanged zeolites, to explain the reactivity order found experimentally.

2. Experimental

2.1. Catalysts

Two samples of HZSM-5, with different Si/Al ratio, were obtained. They were named HZSM-5 (28) and HZSM-5 (82), where parenthesis indicates the Si/Al molar ratio. Table 1 shows some characterization parameters for the samples. The HZSM-5 (82) was obtained from PQ Corporation and the HZSM-5 (28) was supplied by PETROBRAS. Both were checked for crystalline purity and showed a XRD pattern consistent with the ZSM-5 structure.

The HZSM-5 (28) was subjected to an ion exchange with 1 M solutions of zinc chloride at 60 °C for 12 h. Three samples were prepared with nominal zinc exchange of 10, 25 and 50%, relative to the total amount of exchangeable sites.

2.2. Catalytic tests

The catalytic conversion was carried out in a continuous flow, fixed bed unit, coupled on line with a capillary gas chromatograph. The zeolite was firstly pre-treated under flowing air (40 ml/min) at 773 K for 1 h, following a program sequence (room temperature up to 423 K at 2 K/min and then to 773 K at 5 K/min). The reactor was then cooled to 698 K, under flowing nitrogen (20 ml/min) and a flow of chloromethane in nitrogen (8%, v/v) was passed through the catalyst bed. A U-tube packed with BaO was placed just after the reactor to trap the formed HCl. In control experiments, it was shown that neither chloromethane, nor the hydrocarbons were significantly adsorbed on the BaO bed, at room temperature.

The products were analyzed by on line capillary gas chromatography. The space velocity was adjusted by varying the gas flow or the weight of the catalyst used, to control the conversion degree, trying to confine the results with all catalysts, to a narrow conversion range.

3. Results

Table 2 shows the results of conversion and selectivity for the catalysts used. It should be stressed that no appreciable deactivation was found within the time period of the reaction (about 140 min). Although earlier works report [9–11] a strong deactivation during the first 40 min of reaction, we were not able to confirm this trend. A possible explanation was due to the different temperatures, conversion degree and partial pressure of chloromethane used.

It can be seen that propene was the major product on all zeolites. The highest selectivity for propene was found on HZSM-5 (82). Compared with the HZSM-5 (28) production of ethene and propene was significantly higher when increasing the Si/Al ratio. This can be explained in terms of lowering the hydrogen transfer. As the sites become more isolated, the rate of bimolecular reactions is reduced. In fact, propane was only observed on HZSM-5 (28), stressing this hypothesis. Yet, the activity of HZSM-5 (28) was higher than HZSM-5 (82) and might be associated with the higher number of active sites.

On Zn-ZSM-5 the selectivity to light olefins was higher than on HZSM-5 (28). Since both zeolites have the same Si/

Table 2
Catalytic test results of chloromethane conversion on ZSM-5 zeolites at 698 K

	HZSM-5 (28)	HZSM-5 (82)	Zn-ZSM-5 (10%)	Zn-ZSM-5 (25%)	Zn-ZSM-5 (50%)
WHSV (h^{-1})	4.7	4.2	6.6	7.8	11.4
Conversion (%)	25	22	20	22	29
Rate ($10^4\ s^{-1}$)[a]	3.2	2.6	3.7	4.8	9.2
Selectivities[b]					
CH_4	1	–	1	2	1
Ethene	26	13	19	16	19
Propene	43	62	56	54	52
Propane	11	–	–	–	–
$C4^+$	19	25	24	28	28
Ethene + propene	69	75	75	70	71

[a] Assuming differential conditions.

[b] Selectivities after 2 h on stream.

Al ratio, one can conclude that zinc exchange influences the selectivity in the same way as the increase of the Si/Al ratio does. Table 2 also shows that the degree of zinc exchange produces an increase in catalyst activity, especially for higher zinc content. The selectivity to propene is also higher on Zn-ZSM-5. It is well known that zinc exchanged zeolites have dehydrogenation properties [13–15]. In a recent paper [16], it was shown that even methane could be dissociatively adsorbed on Zn-ZSM-5. The Zn^{2+} cations downshift the wavenumber of the C–H stretching vibration, affecting the polarizability of the bond. This might result in heterolytic dissociation of the methane molecule [16]. A similar mechanism might be operating in our case, explaining the better selectivity to propene, as virtually no propane was observed on the Zn-exchanged zeolites.

3.1. Theoretical calculations

The role of zinc exchange in improving the dehydrogenation activity of zeolites has been recognized in the literature. Recent theoretical calculations [17,18] investigated several pathways for this reaction, including the study of different zinc species.

Nevertheless, the results indicated that the zinc also improves the catalytic activity, increasing the rate of chloromethane conversion to olefins. This result indicates that zinc cations play a role in the interaction of chloromethane with the catalyst, lowering the activation energy of the reaction.

To investigate the mechanistic aspects of the reaction and the role of the cation, we performed theoretical calculations on the interaction of chloromethane with MT_6 clusters, where M represents an alkaline cation as well as a proton, for comparison.

The MT_6 cluster comprises five silicon atoms, one framework aluminum atom, seven framework oxygen atoms and an alkali metal cation M, representing a possible active site on the zeolite structure. The valences of the Si atoms were completed with hydrogen atoms and OH groups were used to avoid dangling bonds in the Al atom. The calculations were done at B3LYP/6-31G** level, without imposing any geometrical constraint in the cluster. For K, Rb and Cs cations a relativistic effective core potential (RECP) [19] was used. The geometry of the MT_6 cluster and chloromethane was initially separately optimized. From these optimized geometries, the structures corresponding to the adsorption minima of chloromethane on the MT_6 clusters were obtained. The latter structures were then used in the search for the transition state (TS) for methoxide formation, using the Berny and the eigenvalue following (EF) algorithms. A vibrational analysis was performed for all structures and the frequencies scaled by 0.96, to obtain the zero-point energy (ZPE) and thermal corrections to 298.15 K. Unless otherwise stated, all energy differences refer to enthalpy. All calculations were done using the Gaussian 98 package [20].

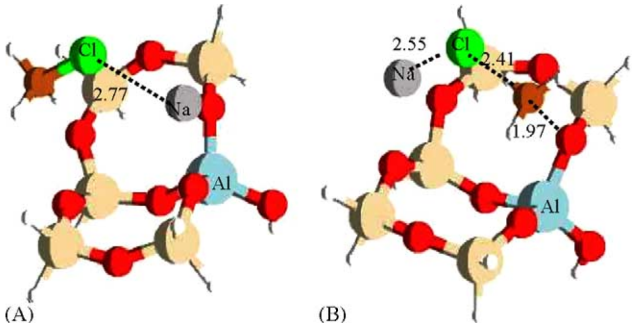

Fig. 1. Adsorption complex (A) and transition state (B) for methoxide formation from chloromethane and NaT_6 at B3LYP/6-31G** level; distances in Å.

Fig. 1 shows the structure of the adsorption complex (physisorption) and the TS for interaction of chloromethane with the NaT_6 cluster. One can see that the adsorption complex involves a charge dipole interaction between the alkali cation and the chlorine atom. Table 3 shows some geometric parameters for the whole MT_6 series. One can see that the M–Cl distance increases on going from Li^+ to Cs^+, reflecting the strength of the ion–dipole interaction. The smaller and harder Li^+ cation demands a stronger and more electrostatic interaction with the chlorine atom, which reflects the lower (more negative) physisorption enthalpy, showed in Table 4. On the other hand, the bigger and softer Cs^+ cation has the largest M–Cl distance among the alkali metal series and the highest (less negative) physisorption enthalpy.

The TS for methoxide formation resembles the TS for a S_N2 like reaction. While the chloride departs from one side, the framework oxygen atom attacks the carbon atom at the opposite site. This behavior was previously shown for the butylchloride interaction with a MT_3 cluster [21].

Table 3 shows some geometric parameters for the calculated TS. One can see that the C–Cl bond stretches on going from the adsorption complex to the TS. On the other hand, the C–O distance decreases, reflecting the nucleophilic assistance in the TS. The LiT_6 showed the largest C–O

Table 3
Main geometric parameters for the interaction of chloromethane with the MT_6 clusters, at B3LYP/6-31G**

Cluster	O–C	C–Cl	O–C–Cl	O–(H/M)	(H/M)–Cl
Adsorption complex					
HT_6	3.96	1.82	113.0	0.98	2.28
LiT_6	3.51	1.83	101.8	1.86	2.42
NaT_6	3.46	1.83	108.2	2.21	2.77
KT_6	3.47	1.82	117.2	2.60	3.22
RbT_6	3.54	1.82	102.3	2.84	3.45
CsT_6	3.48	1.82	114.7	3.09	3.73
Transition state					
HT_6	1.82	2.62	165.4	X	X
LiT_6	1.85	2.57	166.0	X	X
NaT_6	1.97	2.41	170.3	X	X
KT_6	1.80	2.59	173.6	X	X
RbT_6	1.77	2.61	174.8	X	X
CsT_6	1.75	2.62	175.7	X	X

Distances in Angstrom (Å) and angles in degree (°).

Table 4
Energetics of chloromethane adsorption and reaction on the MT_6 cluster, at B3LYP/6-31G**

Initial state	Adsorption complex ΔH (kJ/mol)	Transition state ΔH (kJ/mol)
$HT_6 + CH_3Cl$	−18.1	129.8
$LiT_6 + CH_3Cl$	−47.9	89.5
$NaT_6 + CH_3Cl$	−28.1	100.0
$KT_6 + CH_3Cl$	−31.1	104.2
$RbT_6 + CH_3Cl$	−17.2	120.1
$CsT_6 + CH_3Cl$	−8.4	121.0

distance, while the CsT_6 presented the shortest, reflecting the position of the TS in the reaction coordinates. The results suggest that Li^+ shows an earlier transition state, with less degree of nucleophilic assistance and the Cs^+ shows a later transition state, more dependent on the nucleophilic assistance from the framework oxygen atom.

Table 4 shows the activation enthalpy in relation to the adsorption complex (true activation enthalpy). The Li^+ showed the lowest barrier while Cs^+ showed the highest. A similar behavior was found on the calculation of proton elimination from ethylchloride on a MT_5 cluster [22]. The results reflect the Lewis acid strength of the alkali metal cations. The driving force for methoxide formation is the M–Cl electrostatic interaction in the TS. Hence, the smaller and harder Li^+ cation shows a stronger interaction with the leaving chloride, presenting the lower activation barrier. These calculations are in good agreement with the experimental order of activity for the chloromethane conversion over alkali cation exchanged ZSM-5 [12], offering an explanation for that order, based on the strength of the electrostatic metal–chlorine interaction. The Zn^{2+} cation has electronegativity higher than the Li^+ and an ionic radius between the Li^+ and the Na^+ cations. Thus, it would be reasonable to assume that the electrostatic interaction between the Zn^{2+} cation and the chlorine atom might be of the same order of magnitude or even higher than the Li–Cl interaction, explaining the high activity of Zn-ZSM-5 in converting CH_3Cl.

Tables 3 and 4 also show the results of calculation for the HT_6 cluster. It can be seen that the activation enthalpy was higher compared with all metal-exchanged clusters. Apparently, the driving force for the reaction is the electrostatic interaction between the metal cation and the chlorine atom. Therefore, the protonic zeolite is not so active for chloromethane conversion, as the metal-exchanged zeolites are. This result is in agreement with the experimental results observed in this work for Zn-ZSM-5 and in other studies that used metal-exchanged zeolites [9,12].

4. Conclusions

HZSM-5 and Zn-ZSM-5 zeolites are promising catalysts for converting chloromethane to light olefins, such as ethene and propene, at 698 K. The selectivity to the light olefins increases with increasing Si/Al ratio or the exchange of Zn^{2+} on the catalyst. The Zn-ZSM-5 showed a higher activity and selectivity compared to the protonic zeolite.

Theoretical calculations for the interaction of chloromethane with a MT_6 cluster showed that the activation energy for methoxide formation increases on going from Li^+ to Cs^+. The reaction is governed by the metal cation chlorine electrostatic interaction in the TS, explaining the reactivity order in the alkaline metal series, as well as for the protonic zeolite.

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