Selective monochlorination of methane over solid acid and zeolite catalysts *

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Chlorination of methane was studied over amorphous silica–alumina, silicalite as well as H-mordenite, X, Y, NaL and H-ZSM-5 zeolite catalysts. The heterogeneous transformations were carried out in a continuous flow reactor in the 200–425°C temperature range, under atmospheric pressure (methane to chlorine ratio 4:1, GHSV 600 ml/ g h). Chlorination of methane over zeolites in the 200–300°C temperature range proceeds without selectivity indicating a radical mechanism. Above 300–350°C, depending on the nature of zeolite, selective monochlorination takes place indicating the dominance of an ionic mechanism. H-mordenite was found to give the best monochlorination at the lowest temperature (99.2% CH_3Cl at 350°C). The observed selectivity of the investigated zeolites is strongly time limited. All investigated catalysts lose their selectivity after five hours on-stream due to extraction of aluminum from the framework of zeolites by hydrogen chloride. Amorphous silica–alumina above 350°C also catalyzes ionic chlorination. The chlorination of methane over silicalite proceeds via the nonselective radical pathway at the investigated temperatures.

Keywords: Methane; chlorination; solid acid; zeolites

1. Introduction

Transformation of methane to higher molecular weight hydrocarbons, particularly of the gasoline range, could become one of the most important processes of the petrochemical industry.

Methane conversion to higher hydrocarbons is realized via Fischer–Tropsch syngas chemistry [2], by direct oxidative coupling [3,4] or through monosubstituted derivatives (for example: methanol, dimethyl ether, dimethyl sulfide,

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methyl chloride, methylamine, etc.) [5]. Only the so-called methanol to gasoline (MTG) process has been developed commercially by the Mobil Corp. [6]. In this process methane is first converted to synthesis gas to produce methanol in a conventional Fischer–Tropsch process and subsequently converted to hydrocarbons using the shape-selective ZSM-5 zeolite catalyst.

An alternative to the MTG technology, avoiding syngas production and Fischer–Tropsch process, is the conversion of methane through its halogenated derivatives, such as methyl chloride, over supported bifunctional acid–base catalysts, for example over WO_3/Al_2O_3 [5]. ZSM-5 zeolite, which plays an important role in the MTG process, also shows good activity and selectivity in the case of methyl chloride to hydrocarbon transformation [7]. Metal-exchanged mordenites also are applicable in this transformation [8].

The chlorination of alkanes, discovered by Dumas in 1840 [9], is the oldest substitution reaction. Thermal or photochemical chlorination is a radical process which lacks selectivity and generally yields mixtures of chloroalkanes. In case of methane all four possible chloromethanes are obtained. A typical product distribution of commercial methane chlorination is: 48% methyl chloride, 35% methylene chloride, 14% chloroform and 3% carbon tetrachloride [10]. If methyl chloride is the desired product, a ratio of at least 10:1 methane to chlorine is required [11].

In contrast to radical chlorination, an ionic process favors monohalogenation. Whereas the electrophilic chlorination of alkenes and of aromatics is well-known and industrially utilized, similar reactions of alkanes were only more recently reported. Methane when reacted with SbF_5–Cl_2 in SO_2ClF solution at $-78°C$ gave dimethylchloronium ion. When the reaction was carried out in an autoclave at room temperature with excess methane the gaseous product was methyl chloride with only traces of methylene chloride, but the conversion was low [12]. The heterogeneous catalytic halogenation (chlorination and bromination) of methane was also investigated over supported solid acids (such as FeO_xCl_y/Al_2O_3, $TaOF_3/Al_2O_3$, $NbOF_3/Al_2O_3$, $ZrOF_3/Al_2O_3$, $SbOF_3/Al_2O_3$, SbF_5/graphite, Nafion-H/TaF_5) or supported platinum metal catalysts (Pt/Al_2O_3, $Pd/BaSO_4$). The reactions were carried out between 180 and 250°C, with gas hourly space velocity (GHSV) of 50–1400 giving up to 58% conversions with the selectivity in methyl chloride generally exceeding 90% [13].

Electrophilic halogenation (chlorination and bromination) of aromatics over zeolite catalysts has been well investigated [14–17]. In the case of chlorination of monosubstituted benzene derivatives (chlorobenzene, toluene) zeolites at 50–100°C show high para-selectivity, which depends on the nature of zeolite, as well as the type of cation, the extent of cation exchange, Si/Al ratio and salt modification. In contrast, in the gas phase chlorination of benzene over ZSM-5, mordenite and silicalite at 175°C Huizinga et al. observed mainly addition of chlorine to hexachlorohexanes. They concluded that zeolites and related materials with high Si/Al ratio, as well as pure silica, under the reaction conditions

favor homolytic dissociation of chlorine leading to a radical process [16]. Laszlo et al. reported that zeolites catalyze chlorination of aromatics by sulfuryl chloride (SO_2Cl_2) in the liquid phase [18]. According to their results, the chlorination can be carried out with high selectivity either on the aromatic ring or in the side chain depending on the appropriate choice of the catalyst and the conditions. The side chain chlorination was carried out in presence of UV-light. Thus the zeolites did not necessarily act as real radical initiators rather than promoters.

Preferential terminal chlorination of straight chain alkanes was reported by Turro et al. in the presence of pentasil zeolites (ZSM-5, ZSM-11) [19]. Nonane (0.5 wt%) adsorbed on ZSM-5 was chlorinated for 5 min at 25°C under UV irradiation to give 67% conversion to chlorinated products, 70% of which was terminally chlorinated. In these experiments the zeolites acted not as catalysts but as a molecular sieve.

Relatively little is known about the interaction of chlorine and zeolites. Kim et al. studied the crystal structure of a chlorine sorption complex of partially dehydrated fully Ag^+-exchanged zeolite A by single-crystal X-ray diffraction [20]. They found the Cl–Cl bond length, 2.49 Å, considerably elongated from that of free Cl_2 (1.99 Å). They suggested H^+ bridges between two chlorine molecules and electron-pair donation (charge transfer) to take place between the electronegative O(I) oxygen and the chlorine molecules. It is manifested by the elongated dichlorine bond length that the chlorine molecule is activated in the pores of zeolites.

We now report our studies on the chlorination of methane over some solid acids and zeolites, showing remarkable monochlorination selectivity under appropriate conditions. At the same time our studies also showed that after five hours on stream the selectivity is lost due to the extraction of aluminum from the framework of zeolites.

2. Experimental

2.1. CATALYSTS AND MATERIALS

NaX (12105-S), NaY (11541-S), NaL (4969-S) zeolites and amorphous silica–alumina (12839–S) were purchased from the Strem Chem. Co. Silicalite (13744-92) was a gift from the Union Carbide Co., H-ZSM-5 (MLO-I-297B) was donated by Mobil, with a Si/Al ratio ≈ 70. The hydrogen forms of the X and Y zeolites were prepared by Na^+–NH_4^+ ion exchange with NH_4Cl, followed by decomposition of the ammonium forms at 450°C temperature until ammonia was emerged from the reactor.

Methane (UN-1971) minimum purity 99.0% and chlorine (UN-1017-RQ) minimum purity 99.5% were Matheson products.

2.2. APPARATUS AND EXPERIMENTS

Experiments were carried out in a fixed bed continuous flow reactor (200 × 12 mm glass tube) operating under atmospheric pressure. The reactor was electrically heated during the experiments. The temperature did not deviate by more than −1°C. All exposed parts of the reactor were shielded from light.

The reactor was charged with 5 g catalyst. After pretreatment (1 h at 450°C in dry nitrogen, flow rate 10 ml/min) the reactor temperature was maintained for the specified experiments between 200 and 450°C. Methane and chlorine were introduced with a flow rate of 50 ml/min (600 ml/g h GHSV) by use of flow controllers. The methane to chlorine ratio was 4:1 or varied between 6:1 and 1:2. (Note that the stability of the methane–chlorine mixtures depends on the ratio of the two components and the temperature. Mixtures of 6:1 ratio are stable up to 500°C, of 1:2 ratio only up to 350°C. Above these temperatures spontaneous explosion can occur.)

The products exiting the reactor were collected in a cold trap and analyzed by GC using a 30 meter DB-1 (J&W) capillary column and flame ionization detector.

3. Results and discussion

For comparison we first carried out thermal chlorination of methane over crushed glass. Up to 300°C the conversion was less than 5%; between 300 and 350°C 100% conversion was reached based on chlorine. The product distribution (table 1) is strongly affected by the methane to chlorine ratio. Above 350°C there is no significant dependence on the temperature, there is also only a relatively small change with the methane to chlorine ratio in the 10/1 to 3/1 range (table 2). These results are fairly typical of radical chlorination.

In contrast to aromatic chlorination [16], silica gel does not show any catalytic effect in methane chlorination. Data for alumina (Al_2O_3) are inconclusive because of its instability under the condition of the chlorination reactions. It is

Table 1
Dependence of product distribution on the CH_4/Cl_2 ratio in thermal chlorination at 400°C

CH_4/Cl_2 ratio	Conversion (%)	Product distribution			
		CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
10/1	7.6	75.5	20.4	4.1	0.01
4/1	19.9	71.5	22.6	5.1	0.04
3/1	26.5	68.1	25.5	5.6	0.07
2/1	33.6	51.6	30.5	13.8	4.10
2/1.5	41.6	42.2	33.0	17.9	6.90

Table 2
Conversion and product distribution of the chlorination of methane. I: glass powder, II: silica–alumina, III: silicalite

Temperature (°C)	Conversion [a] (%)			Product distribution (%)											
				CH_3Cl			CH_2Cl_2			$CHCl_3$			CCl_4		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
200	0.3	0.5	1.5	–	–	–	–	–	–	–	–	–	–	–	–
250	1.2	1.6	8.6	–	–	71.6	–	–	23.8	–	–	4.2	–	–	0.4
300	5.4	7.4	16.1	90.2	91.0	59.1	9.0	9.0	30.6	0.6	–	9.8	0.2	–	0.5
350	19.2	17.2	24.1	72.8	93.5	69.7	22.2	6.5	27.4	4.4	–	2.9	0.1	–	–
400	19.9	23.0	24.8	71.5	98.0	75.5	22.7	2.0	23.8	5.1	–	0.6	0.1	–	–
425	19.7	23.2	24.8	70.6	99.0	77.7	24.3	1.0	22.3	5.1	–	–	0.1	–	–

[a] Based on methane ($CH_4/Cl_2 = 4/1$).

Table 3
Conversion and product distribution of the chlorination of methane. IV: H-ZSM-5 zeolite, V: H-mordenite, VI: NaL zeolite

Temperature (°C)	Conversion [a] (%)			Product distribution (%)											
				CH_3Cl			CH_2Cl_2			$CHCl_3$			CCl_4		
	IV	V	VI	IV	V	VI	IV	V	VI	IV	V	VI	IV	V	VI
200	7.1	1.8	1.7	68.3	–	–	24.2	–	–	6.5	–	–	1.0	–	–
250	11.3	7.3	7.5	66.1	82.8	55.3	26.6	17.2	21.1	6.4	–	13.5	0.9	–	10.1
300	16.1	11.8	9.8	61.9	92.7	61.5	34.3	7.3	21.0	3.8	–	9.1	–	–	8.4
350	21.0	19.1	16.2	69.2	99.2	77.2	30.4	0.8	22.8	0.4	–	–	–	–	–
400	25.8	23.5	24.1	87.2	99.8	85.8	12.8	0.2	14.2	–	–	–	–	–	–
425	24.8	–	23.9	92.8	–	90.2	7.2	–	9.8	–	–	–	–	–	–

[a] Based on methane ($CH_4/Cl_2 = 4/1$).

known from the literature that alumina can be chlorinated with chlorinated derivatives of methane ($CHCl_3$, CCl_4) and can also react with HCl. In our experiments we observed $AlCl_3$ to sublime from the reactor.

Results of our studies of the chlorination of methane over zeolite catalysts are summarized in tables 3 and 4. As shown, the product distributions strongly depend on the temperature. Reactions over zeolites give higher conversion than thermal chlorination at 200–250°C, with the product distributions showing considerable similarity to those obtained in radical processes. H-ZSM-5, which was found to possess the highest activity in promoting the radical chlorination of benzene [15], is also the most effective promoter of the radical chlorination of methane at the temperature range of 200–300°C. It is worth noting that L-type zeolite, which gave the best ring substitution results in benzene chlorination, in the case of methane produced the highest chloroform and carbon tetrachloride ratios in the 250–300°C temperature range.

Above 300°C the ratio of higher chlorinated derivatives decreases and at given temperatures over H-mordenite, NaY and NaHY almost selective monochlorination takes place (tables 3 and 4). H-mordenite shows the highest selectivity (99.2%) at the lowest temperature (325°C) (table 3).

The selectivity of monochlorination over the investigated zeolites is, however, strongly time limited (table 5). The time dependence of the chlorination of methane over HY zeolite at 400°C temperature can be seen in fig. 1. The loss of selectivity varies for the different zeolites, but all lose their selectivity after five hours on-stream giving product distributions similar to those of thermal processes.

We also studied the effect of the methane to chlorine ratio. Data obtained for NaHY zeolite are summarized in table 6. With 6 : 1 and 4 : 1 methane to chlorine mole ratios the product distribution is almost identical. With 1 : 2 ratios substantial changes can be observed. The ratio of the higher chlorinated compounds formed via radical reactions is much higher in the whole temperature range. We could not examine methane–chlorine mixtures of 1 : 2 ratios above 350°C because of their explosiveness.

Amorphous silica–alumina is practically inactive below 300°C. Above this temperature it shows similar activity and selectivity as zeolites (table 2), but its deactivation is much faster (table 5).

According to data of tables 3–5 the mechanism of the chlorination of methane over zeolites seems to depend on the temperature. As it is manifested by the product distribution, in the 200–300°C temperature range the reaction seems to proceed via a radical mechanism. Above 325°C temperature, varying on the type of zeolites, the mechanism changes to an ionic one. For instance, the change of the mechanism with increasing temperature over HY zeolite can be seen in fig. 2.

Methane chlorination over silica gel, alumina (Al_2O_3) and amorphous silica–alumina in the 200–250°C temperature range takes place similarly as observed

Table 4
Conversion and product distribution of the chlorination of methane. VII: NaX zeolite, VIII: NaHX zeolite, IX: NaY zeolite

Temperature (°C)	Conversion [a] (%)			Product distribution (%)											
				CH_3Cl			CH_2Cl_2			$CHCl_3$			CCl_4		
	VII	VIII	IX	VII	VIII	IX	VII	VIII	IX	VII	VIII	IX	VII	VIII	IX
200	2.7	4.2	3.6	82.3	85.7	89.1	15.7	14.3	10.9	1.4	–	2.6	0.6	–	–
250	5.8	8.5	9.8	81.7	78.9	75.4	16.3	20.4	22.0	1.3	0.7	2.4	0.7	–	0.2
300	11.1	13.3	12.1	79.4	77.6	78.6	18.4	22.3	20.1	1.9	0.1	1.3	0.3	–	–
350	19.2	21.1	19.7	80.2	76.6	92.4	18.9	21.6	7.6	0.8	1.8	–	0.1	–	–
400	24.5	25.8	24.1	86.9	91.5	98.2	13.0	8.5	1.8	0.1	–	–	–	–	–
425	25.4	25.9	24.9	88.2	92.4	98.8	11.8	7.6	1.2	–	–	–	–	–	–

[a] Based on methane ($CH_4/Cl_2 = 4/1$).

Table 6
Conversion and product distribution of chlorination of methane over NaHY zeolite. A: methane/chlorine ratio: 6:1, B: methane/chlorine ratio: 4:1, C: methane/chlorine ratio: 1:1

Temperature (°C)	Conversion [a] (%)			Product distribution (%)											
				CH_3Cl			CH_2Cl_2			$CHCl_3$			CCl_4		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
200	6.6	6.9	4.0	75.8	77.6	78.4	20.0	18.1	19.0	4.7	3.6	2.6	0.5	0.7	–
250	9.1	11.5	18.5	75.3	77.7	62.8	22.6	21.8	33.7	2.1	0.5	3.5	–	–	–
300	9.6	14.2	20.4	81.3	80.9	60.3	18.3	19.1	34.5	0.4	–	5.1	–	–	0.1
350	11.9	19.1	40.8	92.6	92.5	44.0	7.4	7.5	43.7	–	–	10.6	–	–	1.7
400	15.1	25.5	–	99.4	97.8	–	0.6	2.2	–	–	–	–	–	–	–
425	15.6	24.9	–	99.7	98.8	–	0.3	1.2	–	–	–	–	–	–	–

[a] Based on methane.

Table 5
Product distribution of chlorination of methane after two hours on-stream at 400°C

Catalyst	Product distribution			
	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
amorf. Si–Al [a]	73.7	23.3	2.5	0.5
H-mordenite [a]	69.3	26.3	3.4	1.0
H-ZSM-5	79.8	20.2	–	–
HY	82.2	17.8	–	–

[a] After one hour.

over crushed glass. Silicalite with a crystal structure similar to ZSM-5 zeolite, results in lower conversion but similar product distribution as observed in the case of H-ZSM-5 or HY zeolite at lower temperatures. Zeolites yield about an order of magnitude greater conversion than observed over crushed glass. From these observations one can come to the conclusion that the SiO_2 and Al_2O_3 containing systems with zeolite structure can promote the radical chlorination of methane.

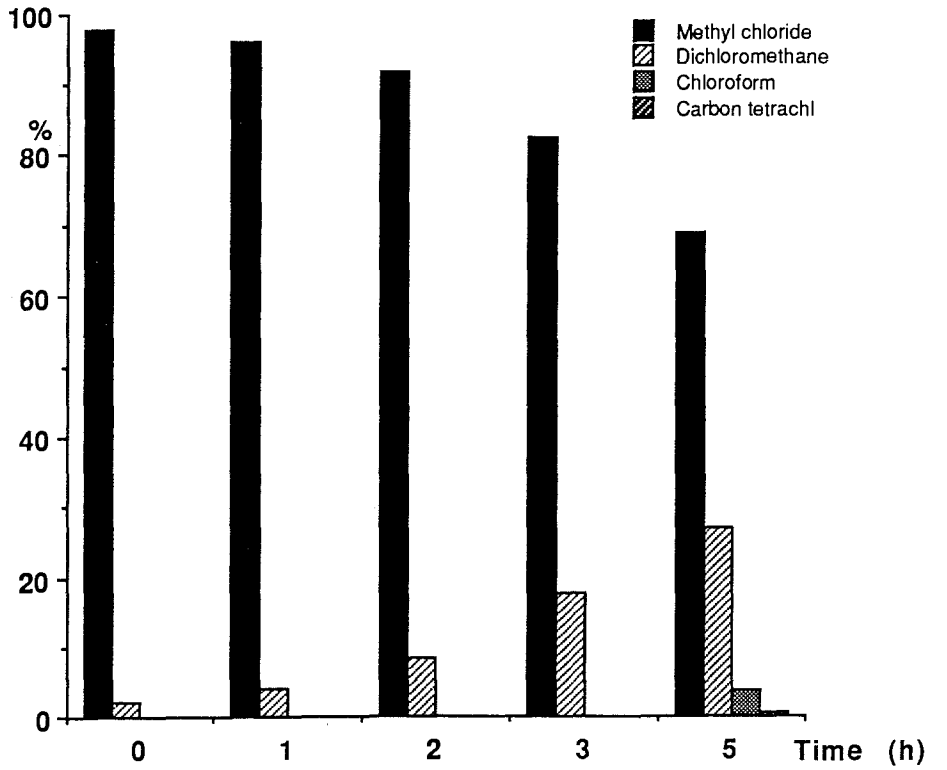


Fig. 1. Time dependence of product distribution of methane chlorination over HY zeolite at 400°C.

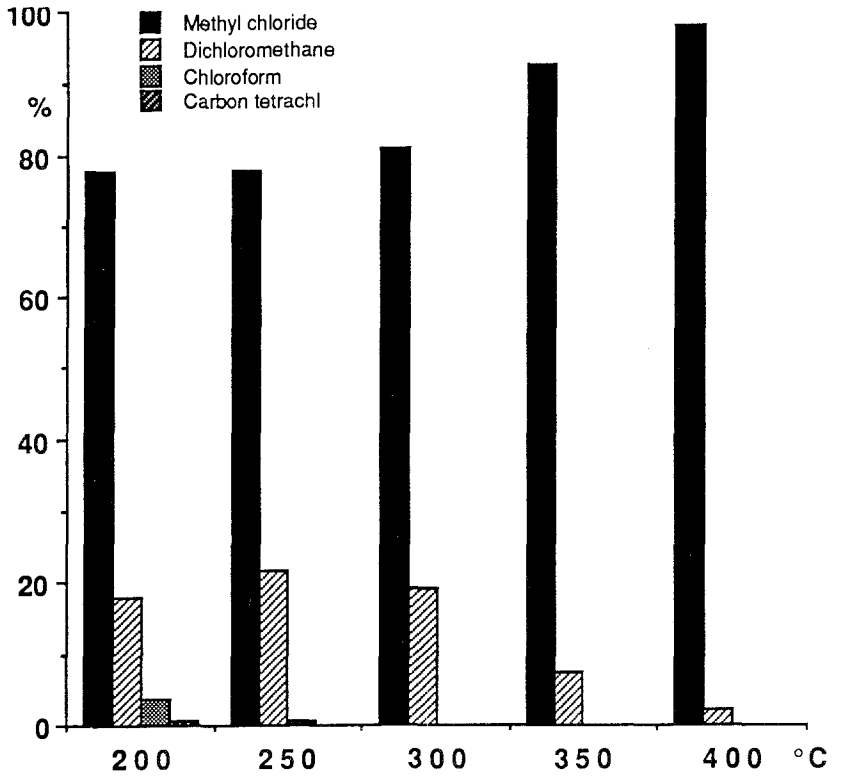


Fig. 2. Temperature dependence of product distribution of methane chlorination over HY zeolite.

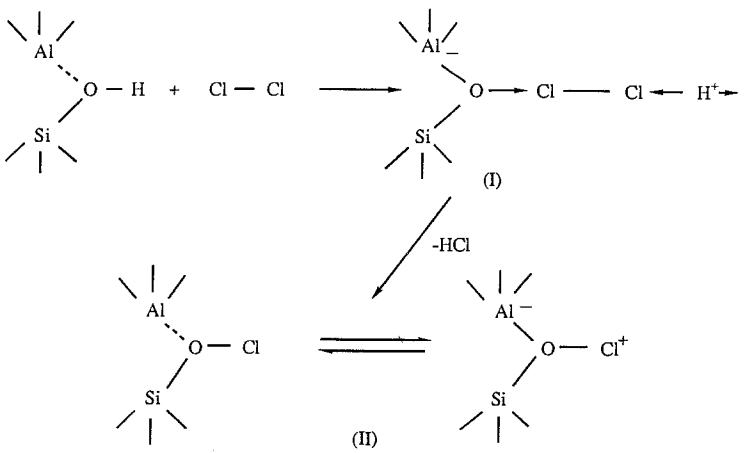
The observed rate increase of the radical process can be the result of a simple kinetic effect. It is well recognized that the concentration of alkanes in the pore structure of zeolites is much higher than in the gas phase. For instance the concentration of *n*-heptane in NaX pores is about 250 times greater than in the gas phase [21]. This so-called concentration effect can increase the rate of the thermally initiated radical chlorination of methane in zeolite pores.

The radical initiation ability of zeolites should also, however, be taken into consideration. It was found in the early study of zeolite catalysis that in the pore structure of zeolites free radicals can build up and can be observed by ESR spectroscopy [22]. By ESR Slinkin et al. could detect free radicals formed from olefins and aromatics over H-ZSM-5 [23] and H-mordenite [24]. They suggested that sites responsible for the formation of radicals involve a redox site and also a Brønsted acidic site [23]. Chang et al. assume assistance of free radicals in the first C–C bond formation in the methanol to gasoline (MTG) process over ZSM-5 [25]. As mentioned, radical chlorination of aromatics was observed over zeolites [16]. Huizinga et al. suggested that homolytic cleavage of chlorine initiates this reaction. Based on the results of Slinkin et al. formation of aromatic radicals could, however, start the reaction. In methane chlorination

formation of chlorine radicals must be the initiation step. Formation of methyl radicals is thermodynamically less favorable under the reaction conditions. Factors which affect the electrophilic catalytic properties of zeolites also show similar effect in case of radical processes. For example, the H-forms show higher activity, the Y forms are more active than the X forms. It seems from these observations that there is a connection between the Brønsted acidity and the radical formation ability of zeolites, as proposed by Slinkin et al. [23].

The electrophilic monochlorination activity of the investigated catalysts is also connected to their acidic properties. Zeolites with higher acidity give better selectivity at lower temperature. For example, H-mordenite qualified as mild superacid by Hall et al. [26] gives the best monochlorination selectivity at the lowest temperatures. The H-form of X-zeolites gives better selectivity than the Na-form. It should be realized that the difference of the selectivity of the Na- and H-forms probably is higher than observed because the sodium form is increasingly transformed into H-form by hydrochloric acid formed during the chlorination. Y-zeolites with higher acidity than X-zeolites also give better selectivity. It is worth mentioning that amorphous silica–alumina which has usually poorer activity in electrophilic transformations than zeolites, gave better results than NaX, HX or NaL zeolites, or even H-ZSM-5. Silicalite, with only low electrophilic activity as a consequence of aluminum contamination of the reagents used in its preparation does not show activity for selective monochlorination.

The reactive electrophilic chlorinating agent in the pore structure of zeolites under the reaction conditions is assumed to be of chlorooxonium ion nature (II) formed from the Brønsted acid sites of zeolites through a transitional form (I) which was observed by Kim et al. in an X-ray diffraction investigation [20] (scheme 1). A similar suggestion was given by Zubakov et al. in the case of bromination of aromatics over zeolites [27]. It is worth to note that the reaction



Scheme 1.

can take place between the methane molecule and either the transitional form (I) or the chlorooxonium ion.

The observed monochlorination selectivity cannot be the consequence of the shape selective property of the zeolites, because the smaller pore diameter of ZSM-5 compared to Y-zeolite would have been expected to give the opposite result.

Whereas the reported results show that selective electrophilic monochlorination of methane is possible over zeolites, the reactivity of zeolites or amorphous silica–aluminas is strongly time limited. All investigated catalysts lost their activity after five hours on stream. It is well recognized that zeolites can lose their aluminum content upon action of strong acids [26]. In presently studied systems hydrogen chloride, formed as a by-product, can dissolve aluminum from the zeolite framework under the reaction conditions. $AlCl_3$ was indeed observed to sublimate from the reactor tube.

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