Chemistry for Sustainable Development **22** (2014) 193–199

UDC 544.473

Methane Chlorination on Fibreglass Catalysts

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(Received December 3, 2013)

Abstract

Gas phase methane chlorination in the presence of fibreglass catalysts has been investigated. It has been demonstrated that increasing the acidity of the glass fibres leads to an increase in the selectivity of the formation of methyl chloride. Unlike zeolite catalysts, the fibreglass catalysts are stable and do not get deactivated during several dozens of hours.

Key words: fibreglass catalysts, methyl chloride, methane chlorination

INTRODUCTION

The stability with respect to the action of hydrogen chloride is a necessary condition for catalysts used in many chemical processes involving elemental chlorine. Among them, there is a novel group of catalysts based on silicate fibreglass materials. It was established [1–3] that the catalysts based on leached fibreglass materials with a low content of metals (Pt, Pd, Ag, Cr, Co *etc.*) are promising for using in many chemical processes, such as the oxidation of methane, propane, butane, SO_2 and nitroaromatic compounds. Furthermore, these catalysts exhibit even a higher activity, as compared to conventional supported catalysts. The catalysts based on fibreglasses are characterized by a high strength, low aerodynamic resistance, improved mass and heat transfer parameters owing to a small thickness of the elementary filaments. These silicate fibre glasses usually have a low specific surface area (1 m^2/g) and do not have mesopores and micropores. However, it was found [1–3], that as a result of specially selected procedures of leaching the fibre glass and the subsequent introduction of a metal, the near-surface volume of silicate fibre glasses exhibit highly-active states of the components applied could form, to all appearance, in the form of metal clusters. At the same time, from the literature, we are not aware of any attempts to use this class of catalysts for the processes accompanied by the evolution of highly reactive hydrogen chloride. In this regard, the reaction of methane chlorination is of interest, since the one of the products of the reaction is presented by methyl chloride, *viz.*, an important chemical intermediate for the production of silicone polymers, *etc.*

Among radical chain reactions the reaction of methane chlorination with molecular chlorine is most comprehensively studied [4–6]. This reaction can be initiated in three ways: photochemical, thermally or catalytically. However, in the course of the implementation of this process, in any case a moment comes, when, despite the presence of a significant amount of unreacted methane, the formation of all four possible chloromethanes begins, due to successive reactions:

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_3Cl_2 \xrightarrow[-HCl]{Cl_2}$$

$$CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4$$

The selectivity with respect to the first product, methyl chloride, is usually relatively low owing to the radical mechanism of the process. The addition of chlorine increases the reactivity of each subsequent product, relatively to the previous one. As the result, the rate of chlorination increases in the series: $CH_4 < CH_3Cl < CH_2Cl_2 < CHCl_3$.

The intensity of the methane chlorination increases with increasing the reaction temperature, contact time and concentration of chlorine. The selectivity of the formation of methyl chloride depends in a complex way on the reaction conditions. In order to obtain methyl chloride with a high yield (about 95 %), the molar ratio of CH_4/Cl_2 should be maintained at least equal to 10 : 1 [7, 8].

Catalysts for the methane chlorination facilitate significantly the process. In particular, it is possible to avoid explosions and the formation of side-products of chlorination.

In contrast to photochemical reactions and thermal chlorination, catalytic chlorination in the presence of solid catalysts does not depend on the presence of the substances, causing the breakage of chains of conversions of free radicals. Heterogeneous catalytic conversions are usually implemented *via* the ionic mechanism, whereby the catalyst causes polarizing the chlorine molecule [6]. Further, the chlorination proceeds *via* the formation of cations when interacting Cl^+ ion with methane molecule.

The authors of [9] investigated the chlorination of methane in the presence of both solid supported acidic catalysts (FeO_xCl_y/Al_2O_3, $TaOF_3/Al_2O_3$, $NbOF_3/Al_2O_3$, $ZrOF_2/Al_2O_3$, $SbOF_3/Al_2O_3$, SbF_5/graphite и Nafion-H/TaF_3), and catalysts containing noble metals (Pt/Al_2O_3 and $Pd/BaSO_4$). For most of the catalysts tested, the selectivity of methyl chloride formation at methane conversion level of 20–30 % and temperature of 250 °C exceeded 90 %. According to the authors of [9], the heterogeneous acidic centers of the catalyst surface polarize chlorine molecules, and the subsequent chlorine attachment to methane is implemented via an ionic mechanism. In other words, the chlorine bound with the catalytic surface, acts as an electrophilic agent that interacts with methane within the framework of a typical substitution reaction.

The authors of [10] investigated the methane chlorination in the presence of an amorphous aluminosilicate such as silicalite and zeolite catalysts such as H-mordenite, X, Y, NaL and HZSM-5. It was found that methane chlorination using these catalysts within the temperature range of 200–300 °C took place with no selectivity. According to [10], this indicates a radical mechanism under the mentioned conditions of the process. At the same time, for the temperature values greater than 300–350 °C there was a selective monochlorination process observed, which process depends on the nature of zeolite, and indicates changing the radical mechanism by the ionic one. The highest selectivity level (99.2 %) with respect to methyl chloride formation was observed for H-mordenite (at 350 °C and at the level of methane conversion equal to 19.1 %). It was found that amorphous aluminosilicate at 350 °C also catalyses the methane chlorination according to the ionic mechanism.

The authors of [11] studied the catalytic methane chlorination in the presence of solid catalysts based on sulphated zirconium oxide. It was found that the modification of such catalysts by platinum cations or by the cations of iron and manganese results in increasing the selectivity level of methyl chloride formation as compared to unpromoted catalysts. The catalyst under investigation retained the activity thereof in the course of the experiment (5–7 h), however at the temperature higher than 225 °C, the catalysts became deactivated due to the formation of volatile promoter metal chlorides under the action of hydrogen chloride. Promoter metals were gradually removed from the catalyst surface to be deposited on cold tubes in the form of corresponding chlorides.

Thus, in the case of using the acidic catalysts a transition is possible from the radical mechanism of methane chlorination to the ionic mechanism, which allows increasing the selectivity level of methyl chloride formation. However, oxide catalysts under the conditions of a corrosive reaction medium are unstable, therefore searching for more stable catalysts is required.

This paper presents the results of preliminary studying the influence of the nature of modified fibreglass materials upon the selectivity level of methyl chloride formation in the reaction of methane chlorination.

EXPERIMENTAL

Preparation of catalysts

We investigated samples made of fibreglass materials subjected to acidic and thermal treatments with platinum compounds deposited thereon. The starting material was presented by a commercial fibre glass (manufacturer “SPC Stekloplastik”) leached with 5 % aqueous sulphuric acid, with fibre diameter amounting to 7–10 μm made of zirconium silicate glass with the following composition (%): SiO_2 81.7, ZrO_2 15.9, Al_2O_3 1.1, Na_2O 0.07, K_2O 0.07, CaO 0.10, Fe_2O_3 0.09. The active component introduced by means of the impregnation of the original fibreglass (FG) by platinum tetrammine solution at a room temperature. The samples were then washed with deionised water in order to remove metal compounds weakly bound with the carrier; further they were dried at 110 °C and calcined in air at 300 °C. Fibreglass samples containing Pt were additionally reduced in a hydrogen atmosphere at 300 °C. The amount of platinum in the FG, measured by means of atomic emission spectroscopy with inductively coupled plasma using a PerkinElmer Optima 4300 DV spectrometer, was equal to 0.02 mass %. The Pt-containing samples prepared by means of this method as well as the original leached sample (FG) were subjected to sulphating *via* treatment with a mixture of steam and gas (10 vol. % SO_2 + 88 vol. % O_2 + 2 vol. % H_2O) at a temperature of 800 °C (samples H-Pt/FG and H-FG, respectively). Sample Pt/H-FG was prepared *via* applying platinum tetrammine onto preliminarily sulphatized fibre (H-FG), followed by heating at 485 °C.

In addition, experiments in the presence of zeolite H-ZSM-5 with Si/Al ≈ 40 and pure silicon structural analog thereof silicalite-1, that were obtained *via* hydrothermal synthesis, were performed [12].

Catalytic testing

The experiments were carried out using a flow-through reactor (a quartz tube 200 mm long with an internal diameter equal to 14 mm) with a fixed-bed catalyst at atmospheric pressure, and heating with an electric tubular furnace within the temperature range of 150–425 °C. To the reactor were placed 5.0 g of catalyst. The samples of fibreglass materials in the form of fluffed filaments were placed into the reactor and compacted to obtain a minimum volume. The samples of H-ZSM-5 and silicalite-1 were used as a powder with a grain size ranging within 0.25–0.50 mm.

Methane and argon with a purity of better than 99.9 % were fed from the cylinders *via* a gas flow regulator. Chlorine was produced by means of sodium chloride electrolysis with the use of graphite electrodes, further it was diluted with argon, dried by passing through a trap with concentrated sulphuric acid to be mixed with methane. The molar ratio of Ar/CH_4 was maintained at the value of 3 : 1. All the technological tubes and the volumes filled with chlorine were isolated from light. The amount of chlorine formed was calculated according to the electrochemical equivalent, and according to the quantity of electricity passed through the saturated sodium chloride solution that served as the electrolyte. The molar ratio of Ar/CH_4 in the initial mixture supplied to the reactor was equal to 3 : 1. The feeding rate of the initial gas mixture amounted to 0.5–2.0 $L/(g_{cat} \cdot h)$.

The composition of the reaction mixture at the inlet and that of the reaction products at the outlet from the reactor were analysed by means of gas chromatography using a Tsvet-570 chromatograph with a flame ionization detector and a quartz capillary column 20 m long and 0.3 mm in diameter.

RESULTS AND DISCUSSION

For all of the samples under investigation we have determined the conversion level of methane and the selectivity level of the formation of chloromethanes, depending on the reaction temperature within the range 150–425 °C. In order to compare the catalytic activity and the selectivity of the samples the experiments were carried out with the molar ratio CH_4/Cl_2 = 3 : 1, whereat the formation of methyl chloride is prevailing as to compare with the formation of dichloromethane and trichloromethane. It is known [8] that in the case of methane chlorination in the gas phase, the

TABLE 1

Effect of the temperature on the conversion degree of methane and selectivity of the formation of the products in the reaction of methane chlorination in the mixture of $CH_4/Cl_2 = 3:1$ on the modified fibreglass catalysts H-FG (I), Pt/H-FG (II), H-Pt/FG (III)

T, °C	Conversion degree of methane, %			Selectivity of the formation of chloromethanes, %											
				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	0.4	1.5	3.2	100	94.5	97.5	–	5.5	2.5	–	–	–	–	–	–
250	1.6	4.2	7.2	96.8	92.3	92.8	3.2	7.7	7.2	–	–	–	–	–	–
300	8.6	12.8	18.9	86.5	79.6	81.6	13.5	18.5	17.5	–	1.9	0.9	–	–	–
350	15.0	17.6	24.3	75.5	71.3	74.5	24.2	25.6	23.7	0.3	3.1	1.8	–	–	–
400	19.4	19.4	24.9	66.4	71.0	71.5	28.9	26.9	26.4	4.5	2.1	2.1	0.2	–	–

Note. Dash means that the product is absent.

composition of products depends on the initial CH_4/Cl_2 molar ratio so that the maximum yield of any individual chloromethane in the mixture of chloromethanes is usually observed at the ratio of reagents that corresponds to the stoichiometry of the formation thereof from the initial substances.

Table 1 demonstrates the results of studying the methane chlorination as a function of temperature (200–400 °C) on fibre glass catalysts H-FG, Pt/H-FG and H-Pt/FG. It is seen that the nature of the catalyst and the sample temperature affect both the conversion level of methane, and the selectivity level of the formation of chloromethanes.

Figure 1 demonstrates the methane conversion level depending on the temperature for these samples as compared to the original FG sample. It is evident that the process of methane chlorination in the sulphated and modified with platinum samples is shifted toward lower temperature values as to compare with the unmodified FG sample. This indicates the fact that the modified fibre glass exerts a catalytic effect. The conversion level of methane in the mixture with the molar ratio of $CH_4/Cl_2 = 3:1$ does not exceed a value about 30 % due to the deficiency of chlorine provided that only methyl chloride is formed. A more profound chlorination with the formation of methylene chloride, chloroform and carbon tetrachloride reduces the conversion level of methane to a more considerable extent. So, at the reaction temperature amounting to 400 °C the most of selectively functioning sample H-Pt/FG exhibit this parameter to be equal to about 25 %, whereas less selective samples Pt/H-FG and H-FG under the same conditions exhibit the value less than 20 %, since a significant amount of the chlorine used in the chlorination reaction is consumed for the consecutive reactions of the chlorination of chloromethanes.

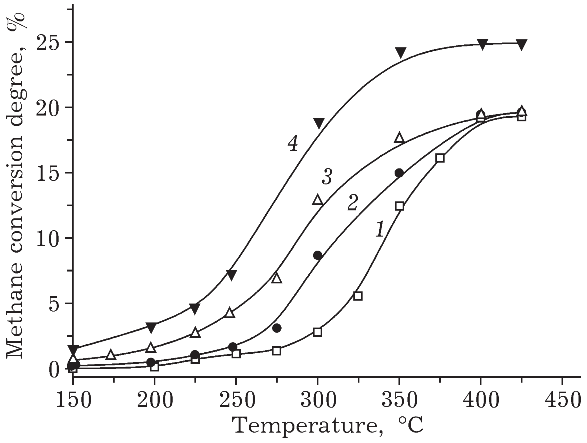

Fig. 1. Dependence of the degree of the conversion of methane from the temperature in the reaction of chlorination of methane in the mixture of ($CH_4/Cl_2 = 3:1$) in the presence of fibreglass catalysts: *1* – FG, *2* – H-FG, *3* – Pt/H-FG, *4* – H-Pt/FG.

The differences in the properties of the samples are clearly visible in Fig. 2, where the results of testing are presented as the plots of the selectivity level of methyl chloride formation (*S*) depending on the of methane conversion level (*X*). The data were obtained by means of varying the temperature of the reactor within the range of 150–425 °C with all other reaction condition being equal (the flow rate of the reagents, their concentration thereof and $CH_4/C1_2$ ratio in the initial mixture, the weighed sample portion).

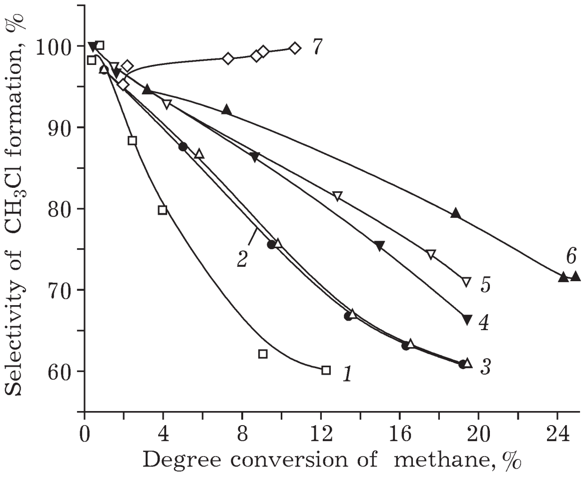

Fig. 2. Dependence of the selectivity of the formation of CH_3Cl from the conversion degree of methane in the reaction of methane chlorination in the mixture CH_4/Cl_2 = 3 : 1 in the presence of catalysts: *1* – silicalite, *2* – hollow reactor, *3* – FG, *4* – H-FG, *5* – Pt/H-FG, *6* – H-Pt/FG, *7* – HZSM-5.

The dependences obtained for all samples are close to a linear function. Starting from almost one point at $S \approx 100$ % at a low conversion level of methane, they diverge like a fan at different angles with respect to the line corresponding to the corresponding the relationship inherent in the radical chlorination in a hollow reactor . The higher is the position of the line, the higher is the selectivity level of methyl chloride formation at the same methane conversion level.

It is known [10] that the highly selective methane monochlorination on the silicalite is impossible, since the trace amounts of aluminum from the reagents used for the preparation of silicalite, cannot form active centres in significant concentrations. On the contrary, the H-ZSM-5 exhibits producing mainly methyl chloride owing to the ability of the acidic centers thereof to generate chloro-oxonium ions. In this regard, as the catalysts we investigated also zeolites H-ZSM-5 and silicalite-1.

Silicalite-1 (see Fig. 2, curve *1*), demonstrated the lowest selectivity level of methyl chloride formation. To all appearance, this could be caused by the fact that the methyl chloride and polychlorinated products can be adsorbed in the channels of silicalite-1 in a stronger manner than the methane, and the chlorination thereof in the pores occurs relatively faster as to compare with the methane chlorination. As the result, the selectivity level with respect to methyl chloride formation demonstrates a decrease.

The maximal selectivity with respect to the formation of methyl chloride is attained for the zeolite H-ZSM-5 (see Fig. 2, curve 7). At a reaction temperature of 400 °C and a molar ratio CH_4/Cl_2 = 3 : 1 in the initial mixture, the methane conversion level amounted to only 12 %. However, the selectivity level with respect to the methyl chloride formation attained almost 100 %, whereas after 5–6 h of operation with the catalyst the value abruptly decreased to amount to 60 % and the conversion level of methane at the same time increased up to 20–25 %. To all appearance, the high selectivity level of methyl chloride formation in the presence of H-ZSM-5 could be caused not only by the presence of acidic centers, but also by other factors such as the consumption of chlorine for removing the aluminum atoms from the zeolite framework under investigation. Increasing the CH_4/Cl_2 ratio could lead to an increase in selectivity level with respect to methyl chloride and to decreasing the conversion level of methane. A short lifetime of sample H-ZSM-5 in the course of operation at an elevated temperature could be, to all appearance, connected with destructing the zeolite framework. Such a situation is described by the authors of [10], who observed the zeolite catalysts to exhibit an abrupt decrease of the selectivity level after several hours of operation in a continuous mode owing to the extraction of aluminum from the zeolite framework by hydrogen chloride formed during the reaction.

The selectivity level of methyl chloride formation depending on the methane conversion level for the gas phase chlorination is presented by curve *2* (see Fig. 2). In case of the unmodified sample FG, the observed selectivity with respect to methyl chloride almost coincides with selectivity obtained for the gas-phase chlorination in a hollow reactor.

According to the character of this relationship the modified samples H-FG, Pt/H-FG and H-Pt/FG (see Fig. 2, curves *4*–*6*, respectively) occupy an intermediate position between the original FG sample and H-ZSM-5.

It is believed that the acidic centers in the original fibreglass sample FG are not strong enough for the polarization of chlorine molecules and subsequent methane chlorination via ionic mechanism. When sulphating original FG containing ZrO_n fragments in the structure [11], one could expect appearing strongly acidic centers due to pulling of the electron density from the oxygen atoms by sulphate anions in ZrO_n fragments. Comparing dependences of the selectivity of the formation of CH_3Cl on the degree of the conversion of CH_4 for FG and H-FG samples (see Fig. 2, curve *3* and *4* respectively), one could find that the selectivity for H-FG with respect to methyl chloride increases due to appearing the active centers for chlorination of methane according to the ionic mechanism. Fibreglass carriers have a very low surface area, but they can stabilize the dispersed particles of applied metal in the bulk of glass. In this case, stabilized platinum particles are in a positively charged state rather than in the metal state [3], which, to all appearance causes their high catalytic activity. The application of platinum onto sulphated fibre glass surface (sample Pt/H-FG) is accompanied by increasing the activity (see Fig. 1) and the selectivity level of methyl chloride to a lesser extent than the sulphated fibre glass with platinum already applied thereon H-Pt/FG) (see Fig. 2, curves *5* and *6*). It is obvious, that the sequence of treatment significantly affects the formation of the active surface of fibre glass. It could be believed that the platinum salt solution used in the process of impregnation and the subsequent extraction of the sample in hydrogen either modify or neutralize Brønsted acidic centers, formed as the result of the sulphated treatment of H-FG. So, at the level of methane conversion amounting to 10 % selectivity level with respect to methyl chloride for the fibreglass catalysts exhibits an increase in the following order (%): FG 75.4, H–FG 84.0, Pt/FG 85.2, H–Pt/FG 89.1. Such a significant increase in the contribution of monochlorination as compared with the formation of other chloromethanes could be attributed to appearing qualitatively new acidic sites in the structure of the modified fibre glass.

CONCLUSIONS

Preliminary studies of the reaction of methane chlorination in the presence of modified fibreglass materials indicate the possibility of producing catalysts for processes occurring with the participation of corrosive gases, such as chlorine and hydrogen chloride.

Owing to specific applying active components onto fibreglass materials, the catalysts obtained in the course of the chlorination reaction at the same conversion degree of methane demonstrate show a higher selectivity with respect to the formation of methyl chloride, as compared to unmodified fibre glasses. Taking into account a high chemical resistance of the fibre glasses in the reaction medium containing chlorine and hydrogen chloride, catalysts based on them are more attractive than conventional oxide catalysts.

It has been found that catalytic properties of the studied samples of fibre glasses when contacting with the reaction medium depend from the method of their acidic treatment. According to current ideas, the methane chlorination reaction on heterogeneous catalysts proceeds according to the radical or ionic mechanism, depending on the state of the active surface of the catalyst [13]. Based on this, it could be assumed that as a result, acidic centers capable of methane chlorination via the ionic mechanism are formed on the surface of fibre glasses. Consequently, at least, a part of methane in the presence of modified fibre glasses is chlorinated according to the ionic mechanism, which promotes increasing the selectivity of methyl chloride formation.

Thus, catalysts based on fibreglass materials, stable under the conditions of corrosive environment could be promising for using them in the process of methane chlorination.

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