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Application of Halogens as Catalysts of CH_4 Esterification

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Abstract The aim of our work was to examine halogens as the catalysts of methane esterification in oleum. The experiments were performed at 160 °C in oleum containing 25 wt% SO_3, at methane pressure of 4.27 MPa. A mathematical model including the impact of the catalyst concentration on the initial reaction rate was proposed. The solubility of elemental iodine in 25 wt% oleum at 160 °C was found to be ca. 17 mmol/dm^3.

Keywords Methane · Esterification · Functionalization · Methanol · Methyl bisulfate · Iodine

1 Introduction

The conversion of methane to methanol is currently carried out in a two-step process. Methane is first reformed in a heterogeneously catalyzed process that is energy- and capital-intensive, to produce synthesis gas (a mixture of CO and H_2). Finally the CO and H_2 react at high pressure in a second step to produce methanol.

For the five-year period beginning in 2008, nearly 26 million tons of new capacity of methanol has been announced in an industry with an average demand of about 47 million tons per year across the same timeline [1]. Methanol is used to produce formaldehyde, methyl *t*-butyl ether (MTBE), acetic acid, solvents, chloromethanes, methyl methacrylate, methylamines, glycol methyl ethers, dimethyl terephthalate, antifreeze, and fuels.

There is considerable interest in finding ways to synthesize methanol directly from methane. Several studies have recently shown how this might be done. For example, gas-phase selective oxidation, heterogeneous selective oxidation (450–700 °C, 1–10 MPa). These processes operated by a free radical mechanism, are difficult to control. Among most of the attempts only low yields (>2%) have been reported [2–5].

However, one particular high-yield system for the catalytic conversion of methane to methanol was published in 1993 [6]. In this system a homogeneous reaction takes place in concentrated sulfuric acid and is catalyzed by mercuric sulfate, $HgSO_4$. The desired intermediate reaction product is methyl bisulfate (CH_3OSO_3H), which is separately hydrolyzed to methanol.

Afterwards platinum [7] and iodine [8, 9] catalysts have been reported for the direct, low-temperature, oxidative conversion of methane to a methanol derivative using the same reaction concept as with $HgSO_4$. These processes have the potential of being more energy-efficient because they bypass the energy-intensive step of synthesis gas formation.

These catalysts in oleum have been found to be highly efficient and highly selective, with up to 92% yields of methanol (in the form of methyl bisulfate that can be hydrolyzed later) [5].

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The functionalization of methane over this catalyst system proceeds according to the overall stoichiometry represented by reaction:

$$CH_4 + 2SO_3 \rightarrow CH_3OSO_3H + SO_2 \quad (1)$$

This reaction has been reported to occur with formation of by-product:

$$CH_4 + 6SO_3 \rightarrow CO_2 + 4SO_2 + 2H_2SO_4 \quad (2)$$

Some authors suppose that hydrogen bisulfate is formed from sulfuric acid and sulfur trioxide:

$$CH_4 + H_2SO_4 + SO_3 \rightarrow CH_3OSO_3H + H_2O + SO_2 \quad (3)$$

It is very likely but water reacts immediately with sulfur trioxide

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (4)$$

Combining the Eqs. (3) and (4) the net reaction can be shown to be the (1). The (2) reaction can be formally written as a three-step sequence of: (5), (6), and (4) reaction.

$$CH_4 + 2SO_3 \rightarrow HCHO + 2SO_2 + H_2O \quad (5)$$

$$HCHO + 2SO_3 \rightarrow CO_2 + 2SO_2 + H_2O \quad (6)$$

Dimethyl sulfate besides methyl bisulfate can be produced:

$$CH_4 + CH_3OSO_3H + SO_3 \rightarrow CH_3OSO_3CH_3 + H_2O + SO_2 \quad (7)$$

Methanol can be produced from CH_4 and SO_3 as well [10–12]. Methane is reacted with SO_3 to form methanesulfonic acid (MSA) at 75–80 °C using a free-radical initiator as the solvent. MSA is then oxidized by SO_3 at 160 °C to produce a mixture containing methyl bisulfate and some methyl methanesulfonate. After hydrolysis methanol is obtained.

The aim of our work was to examine halogens as catalysts of methane functionalization in oleum. Periana et al. [9] and Gang et al. [8] have used iodine and other halogens in oleum. The former used weak oleum ($\leq$2.5 wt% SO_3) but high temperature (195 °C) and they made only preliminary investigation. The latter carried detailed research including the kinetics but they used much more concentrated oleum (65 wt% SO_3) and temperature of 170–190 °C.

In an industrial process based on the above mentioned method it would be very important to use oleum containing not much sulfur trioxide. Low temperature would be an advantage. It was decided to carry out the reaction at 160 °C in oleum containing 25 wt% SO_3. The study was focused on the influence of the catalyst concentration the reaction rate and the ester yield. A mathematical model, which includes the impact of the catalyst concentration on the initial reaction rate, was proposed.

2 Experimental

2.1 Reactor

The reaction between methane, sulfuric acid, and sulfur trioxide was performed in a batch reactor. The PTFE lined stainless steel autoclave was used. A PTFE-covered magnetic-drive stirrer and thermocouple pocket were used to minimize the contact of the reactants with the stainless steel walls. The effective volume of the vessel was 0.250 cm^3 for the gas and liquid together. Electronic meters measured temperature and pressure. The pressure data of the reactor was recorded automatically by a computer and a pressure–time graph was displayed on a PC simultaneously.

The volume of the reactor system consists of the volume of the reactor cup, the volume below the reactor lid, and the volume inside the gas tubing. This volume is reduced because of volume of the PTFE-covered magnetic-drive stirrer and the thermocouple pocket. Therefore, series of experiments were designed to determine the actual volume. The reactor was pressurized with methane or nitrogen. After the pressure remained constant, indicating no leakage in the system, the outlet valve was opened. The outlet was connected with a pipe. The volume of the pipe was known. On the basis of pressure-drop measurements the reactor volume was calculated. The van der Waals equation was used in calculations. The volume based on ten measurements averaging 0.250 ± 0.002 dm^3 was found.

2.2 Experimental Procedure

The 100 cm^3 of oleum (25 wt% SO_3) was poured into autoclave. Then the catalyst was added. As the catalysts I_2, KI, KBr, KCl, NaCl, HCl were used.

In order to remove the air, methane was passed through the reactor for 15 min. The valves were closed and temperature was increased up to 160 °C. Thereafter the reactor was pressurized with the methane up to 4.56 MPa (4.27 MPa methane partial pressure). The content of the reactor was stirred with the magnetic stirrer. After a certain reaction time the stirring was stopped and the reactor was water-cooled down to room temperature.

The outlet valve of the reactor was opened and the generated gasses were sampling for gas chromatographic analysis. The analysis was performed with a GC equipped with a thermal conductivity detector. Hydrogen was used as the carrier gas. The HaySep T column was applied.

The liquid content of the reactor was analyzed by a ^{13}C NMR spectroscopy. The ^{13}C NMR measurements were performed using DMSO-d6 as an external lock.

The liquid mixture was transferred in to dropping funnel and dropped slowly into the water. Two volumes of water used per one volume of the liquid. Methyl ester was transformed to methanol. After hydrolysis only the methanol was observed by means of ^{13}C NMR spectroscopy (no methyl ester was present). Methanol was quantitatively analyzed by the mentioned above GC.

It is worth to say that the SO_3 pressure of 25 wt% oleum in the reactor was found to be 0.29 ± 0.02 MPa at 160 °C.

The I_2 pressure was also examined. A small excess of I_2 was added to oleum and heated up to 160 °C in the closed reactor. No significant difference in the pressure with or without iodine was observed. This indicated that the amount of I_2 in the vapor phase probably was small enough to be neglected. This phenomena was observed also by Gang et al. [8].

3 Result and Discussion

Figure 1 shows the ^{13}C NMR spectra of liquid mixture after 20 h of methane and oleum reaction at 160 °C. Iodine (17 mmol/dm^3) was used as a catalyst.

Considering the difficulties in the interpretation of the NMR spectra measured in fuming sulfuric acid, the obtained spectra were compared with the spectra of reference samples prepared as described in [13]. Comparative analysis indicated that the 60.8 ppm signal represents hydrogen bisulfate, which is the only liquid product. Dimethyl sulfate was not formed.

Figure 2 shows a typical plot of methyl bisulfate yield versus reaction time. The yield was calculated on the basis of the pressure–time graph. The pressure changes due to the reactions (1) and (2) and because of SO_3 partial pressure depending on the oleum concentration. The yield of CO_2 was very small (below 1%), so the reaction (2) effect can be neglected. Due to the relatively high pressure applied in the experiments, the van der Waals equation was used in the calculations of states instead of the ideal gas law.

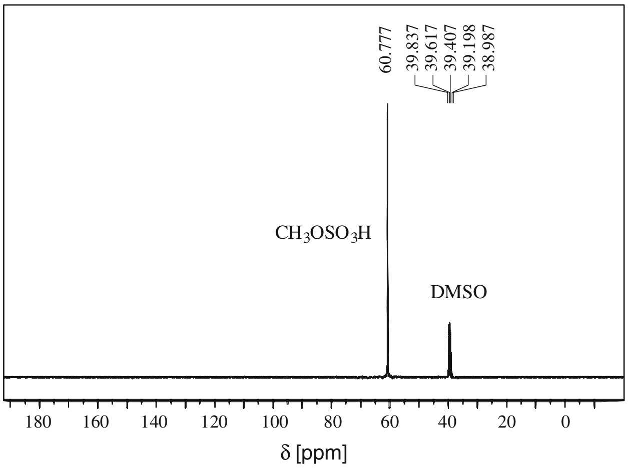

Fig. 1 ^{13}C NMR spectrum (100.6 MHz, DMSO-d$_6$—external lock and reference) after 20 h methane with oleum reaction at 160 °C, methane pressure 4.27 MPa, oleum (25 wt% SO_3) 17 mmol/dm^3 I_2

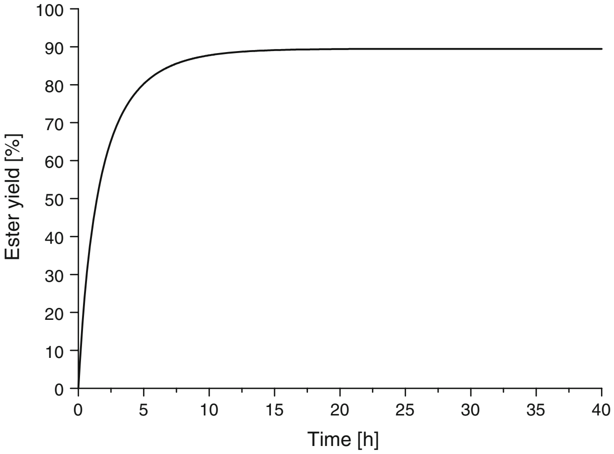

Fig. 2 Methyl bisulfate yield versus time of the reaction. Methane pressure 4.27 MPa, temperature 160 °C, I_2 concentration 17 mmol/dm^3

After the reactor is pressurized with CH_4 the reaction proceeds very fast. Although the rate of the reaction is slower after about 2 h, the reaction is still on. Finally reaction equilibrium is reached and the yield curve becomes flat.

The effects of the concentration of iodine on the yield after different time intervals (2, 22, and 70 h) are presented in the Fig. 3. The reaction conditions were kept constant in each experiment except the concentration of the catalyst.

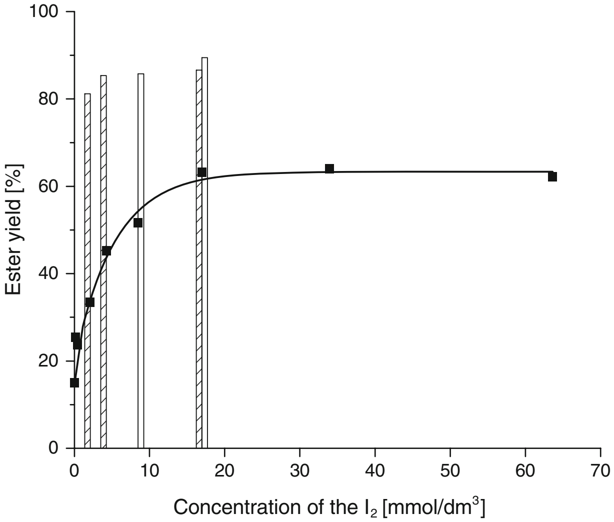

Fig. 3 Methyl bisulfate yield versus I_2 concentration. Methane pressure 4.27 MPa, temperature 160 °C, time of the reaction (■) 2 h, (*striped bar*) 22 h (*plain bar*) 70 h

The catalyst concentration is defined as a milimole of the catalyst in 1 dm^3 of the reaction liquid.

After reaction time of 2 h the methyl bisulfate yield is growing with increasing concentration of the catalyst up to 17 $mmol/dm^3$. Although the concentrations of iodine are different, the concentration of ester reaches the same value if the reaction time is long enough.

This phenomenon confirms iodine to be undoubtedly the catalyst hence the reaction equilibrium is independent of the catalyst amount. When the other conditions remain the same, increasing the amount of the catalyst results in a faster reaction rate and therefore a shorter reaction time to reach the reaction equilibrium.

When the concentration of iodine is higher than 17 $mmol/dm^3$ the reaction rate does not increase with the increment of the catalyst concentration after this point. This is most probably due to the fact that the oleum is saturated with iodine from and after this point. In other words, the solubility of iodine in oleum at the given conditions can be found according to this turning point corresponding to a solubility of iodine in 25 wt% oleum at 160 °C of ca. 17 $mmol/dm^3$. The other authors notice the same [8]. A similar phenomenon was observed in our earlier work [14]. The solubility of the catalyst (Pd) in oleum was investigated. It was found that when the saturated solution was made the increasing of the catalyst amount did not affect the methyl bisulfate yield.

By treating the data of ester concentration versus time at different iodine concentrations (figure is not presented here) the initial reaction rates were found. Figure 4 shows the initial reaction rate–iodine concentration relationship. The initial reaction rate increases with iodine concentration up to about 17 $mmol/dm^3$. After reaching 0.30 mmol/(dm^3 s) the reaction rate remains constant and does not depend on the amount of the catalyst.

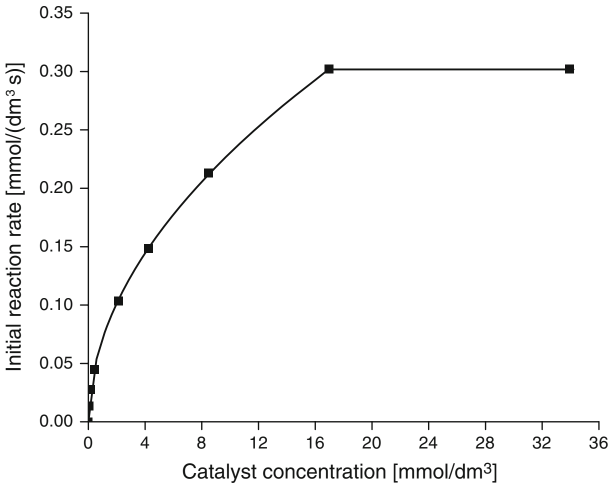

Fig. 4 Initial reaction rate versus I_2 concentration. Methane pressure 4.27 MPa, temperature 160 °C, time of the reaction 2 h

The mathematical model found to best fit the curves on the Fig. 4 is

$$r_i = A \cdot C_{\mathrm{Cat}}^{B}$$

where r_i is the initial reaction rate [mmol/(dm^3 s)] and C_{cat} is the concentration of the catalyst [$mmol/dm^3$]. Similar model was proposed by Gang et al. [8].

The best fitting parameters were found by means of a suitable software (Origin Pro 7.5) based on nonlinear regression method and are reported below.

$$A = 0.0712 \pm 0.0002$$
$$B = 0.51 \pm 0.01$$
$$R^2 = 0.999$$

It is worth to say that Gang et al. [8] obtained the same values for B. Although they used more concentrated oleum (e.g., 65% SO_3) the reaction order of iodine concentration dependence of initial reaction rate was reported as 0.5. We agree with their conclusion that the stoichiometry coefficient of iodine in catalytic reaction might be 0.5 and an intermediate containing only one iodine atom is formed. We would guess that the mechanism of methane activation in 25 wt% and in 65 wt% oleum is the same.

Gang et al. [8] got the value of $A = 0.0114$ but they defined initial reaction rate as the pressure slope [bar/s]. Taking into consideration this definition and volume of the oleum we can guess that in our equation the Gang's value of A supposed to be 1.01. The initial reaction rate in our experiments was slower but we used less concentrated oleum (e.g., 25 wt% SO_3) and lower temperature (160 °C). In an industrial process based on the above mentioned method it would be very important to use oleum containing not much sulfur trioxide. The lower temperature would be an advantage. Of course the methyl bisulfate yield has to be sufficiently high. In experiments described above after 2 h the ester yield reaches 62% (Figs. 2 and 3).

In order to check the other source of iodine, KI as a catalyst was used. As shown in Fig. 5 methyl bisulfate yield decreases with the increasing amount of KI. The reason of this surprising tendency is fast exothermic reactions:

$$KI + H_2SO_4 \rightarrow HI + KHSO_4 \tag{8}$$

$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O \tag{9}$$

Because of raising the temperature of the oleum the sulfur trioxide evaporated what was observed as white fumes. Water formed in the reaction (9) reacts with sulfur trioxide. These are the reasons of the oleum concentration decreasing and falling of the ester yield. Gang et al. [8] did not observe this phenomena but they used more concentrated oleum so the loss of SO_3 was relatively lower. Because bromine and chlorine are usually more

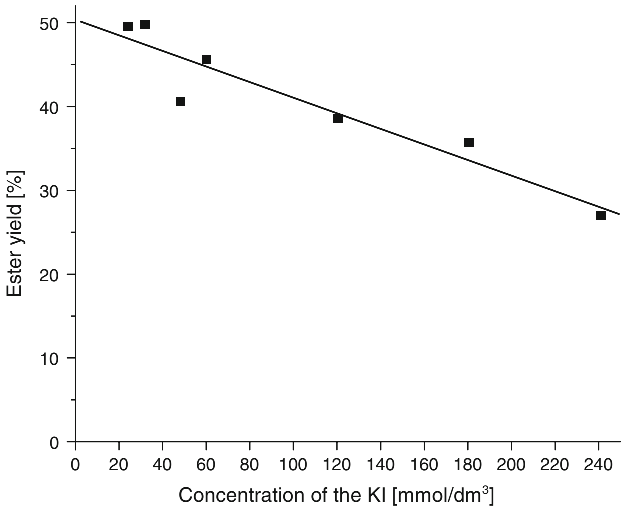

Fig. 5 Methyl bisulfate yield versus KI concentration. Methane pressure 4.27 MPa, temperature 160 °C, time of the reaction 2 h

reactive than iodine we used KBr, KCl, HCl as the catalyst as well.

Figure 6 shows a plot of methyl bisulfate yield versus potassium bromide concentration at different reaction time.

When the KBr is used as a catalyst the ester yield is much lower in comparison with I_2. KCl and HCl do not catalyze the methane functionalization. When KCl and HCl were used no production of ester was observed.

The reactivity of halogens diminishes in the sequence $Cl_2 > Br_2 > I_2$. We have found that the catalytic activity changes in the order: iodine > bromine > chlorine. This phenomenon is opposite to the well known reactivity. Halogens are strong oxidizing elements. Generally their compounds are formed either by gain of one electron to give X^- or by sharing one electron in a covalent single bond.

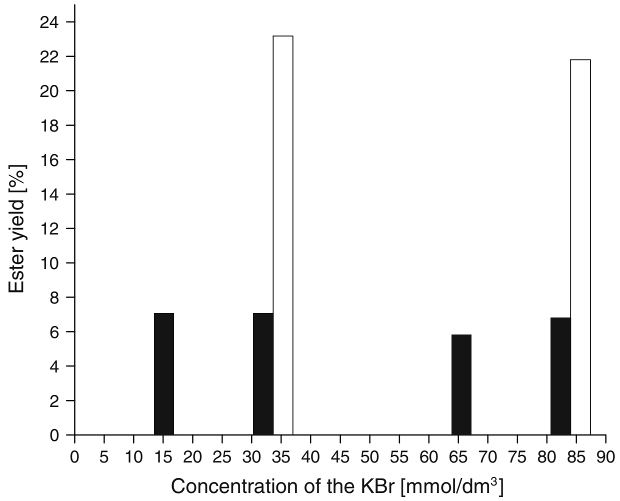

Fig. 6 Methyl bisulfate yield versus KBr concentration. Methane pressure 4.27 MPa, temperature 160 °C, time of the reaction (■) 2 h and (□) 22 h

On the basis of the type of iodine salt used in the experiments, Periana et al. [8] concluded that either I^+ or $I_2{}^+$was the catalyst and ruled out $I_3{}^+$ and $I_4{}^+$; however, it appears that they favored $I_2{}^+$ as the catalyst on the basis of the results of experiments in which $I_2{}^+$ precursors were used. Davico [15] suggested that the catalyst in the activation of the C–H bond in methane is I^+ and not $I_2{}^+$. Our and Gang's [8] kinetics observations are in very good agreement with this theory. We believe that methane activation is catalyzed by I^+. One would expect that other halogen cations such as Br^+ and Cl^+ be able to catalyze methane oxidation. By reason of electronegativity order of halogens the tendency for I_2 to give I^+ ions in solution is also much greater than for the other halogens. Because of it bromine is less active as a catalyst than iodine and chlorine is inactive.

4 Conclusions

The experimental results show that I_2 is an effective catalyst in the direct oxidation of methane to methyl sulfates in 25 wt% oleum at 160 °C, at 4.2 MPa methane pressure. The solubility of iodine in 25 wt% oleum at 160 °C is around 17 mmol/dm^3.

We have found that in the iodine catalytic reaction the initial reaction rate shows a 0.5 order dependence the iodine concentration in 25 wt% oleum. This value is the same as was found for 65 wt% oleum [8].

The order of catalytic activity of iodine, bromine, and chlorine is opposite to usual chemical reactivity.

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