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Methane Conversion to Methanol in Condensed Phase[1]

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Abstract—The subject of our investigations was the oxidation process of methane to organic oxygenates. The catalytic system proposed by us in which palladium occurs in the form of palladium powder dissolved in oleum has not been described up to now. Methanol was obtained by the transformation of methane into methyl bisulfate. Subsequently, methanol was formed as a result of ester hydrolysis. The reaction temperature was varied in the range of 70–190°C; the time was changed from 1 to 20 h. The reaction products were carbon dioxide, methanol, and traces of formaldehyde. We found that the rate of ester formation depends on the partial pressure of methane, the concentration of free sulfur trioxide in sulfuric acid, and the concentration of ester itself in the reaction mixture. An equation for the rate of formation of the methyl bisulfate was proposed. The rate constants were determined by Marquardt's method.

Methane selective oxidation towards methanol or formaldehyde is a scientific challenge and of utmost practical importance. Currently, many researchers are addressing this problem, studying the effect of catalysts, pressure, temperature, kind of oxidant, composition of the reaction mixture, a contact time, etc., on the resulting products.

In the process of the partial oxidation of methane, the metallic oxides [1–3] and other kinds of compounds [4–6] were used as catalysts. Formaldehyde and carbon oxides were found to be the primary oxidation products when studies were performed at atmospheric pressure and 400–600°C. The formaldehyde yield was a few percent. Only conditions of elevated pressure allow one to obtain methanol. The pressure at which the studies were carried out varied in the range 0.5–138 MPa at 400–600°C [7–12]. The methanol yield was a few percent as well.

The oxidation of methane by platinum salts in solution, i.e., via homogeneous catalysis, was first reported in the 1970s by Shilov [13] and coworkers. It was demonstrated [14] that in an aqueous medium, the Pt(II) ion will activate the C–H bonds of various substrates including methane, resulting in their oxidation. Methanol was obtained from methane at 100°C in aqueous solution when Na_2PtCl_4 and Na_2PtCl_6 were added.

The reaction of methane with palladium (II) acetate in trifluoroacetic acid was shown by Sen [15]. The reaction utilized palladium as a reactant not as a catalyst. Methyl trifluoroacetate was obtained with a yield of 60% based on palladium.

Vargaftik *et al.* [16] discloses that, although palladium is an ineffective catalyst for the conversion of methane, Co(III) can be used for this reaction. Methane has been oxidized stoichiometrically by cobalt (III) trifluoroacetate in CF_3CO_2H solution at 150–180°C and 1–4 MPa to give methyl trifluoroacetate. In the presence of oxygen the reaction becomes catalytic with respect to the cobalt(III) salt.

A later publication by Sen [17] discloses a catalytic system using palladium as the catalyst, peroxytrifluoroacetic acid and trifluoroacetic anhydride as the solvent. Only 5.3 turnovers of Pd were observed.

Periana *et al.* [18] show in the WO patent a new method that utilizes acids, oxidizing agents, and catalysts comprising a Class “B” metal from the Mendeleev table and/or Pearson “soft” and “borderline” metal cations which do not undergo one-electron reductions while they do undergo two-electron reductions. The reaction may take place at low pressures and temperatures. The preferred metal catalysts are selected from Pd, Tl, Pt, Hg, and Au. The preferred oxidizing agents are O_2, H_2SO_4, SO_3, and HNO_3. Alkane is converted to an oxy-ester of the acid that is relatively inert to further oxidation under the reaction conditions. The oxy-esters may be converted to alcohols. This step may be used to regenerate the acid for recycling and reuse in the first step.

The authors of the patent recommended a mercury- [19] and platinum-catalyzed [20] high yield system for the oxidation of methane to methanol. They used $HgSO_4$–H_2SO_4 catalytic to methane oxidation to methanol via methyl bisulfate. The reaction catalyzed by mercuric ions is the oxidation of methane by concentrated sulfuric acid to produce methyl bisulfate, water, and sulfur dioxide. At a methane conversion of 50%, 78% selectivity to methyl bisulfate (43% yield) was achieved at a molar productivity of 10^{-7} mol ml^{-1} s^{-1} and a Hg(II) turnover frequency of 10^{-3} per second. The reaction conditions: 180°C, 3.45 MPa of methane.

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[1] This article was submitted by the authors in English.

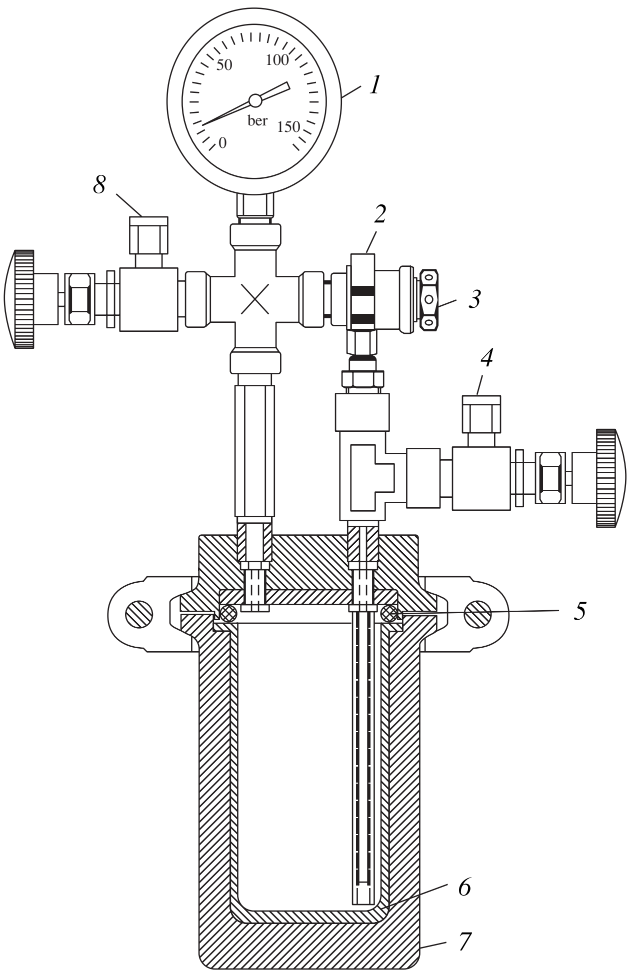

Fig. 1. Autoclave used for methane esterification. (*1*) Manometer, (*2*) thermocouple, (*3*) safety valve, (*4*) inlet, (*5*) PTFE O-ring, (*6*) PTFE liner, (*7*) pressure vessel, (*8*) outlet.

Periana's other catalyst [20] was a platinum complex with 20% oleum. Platinum complexes from the bidiazyne ligand family were stable, active, and selective for the oxidation of a carbon–hydrogen bond to produce methyl esters. At 180–220°C and 3.45 MPa of methane, they generated methyl bisulfate in 72% yield at 81% selectivity and 90% methane conversion.

Other examples for such a type of catalytic system are the following: mercury and palladium sulfates in fuming sulfuric acid [21] and $EuCl_3$-Zn–CF_3CO_2H [22, 23]. The reaction products were appropriate esters that can be readily transformed into methanol via hydrolysis.

EXPERIMENTAL

We developed a palladium–oleum catalytic system for the direct low temperature, selective oxidation of methane to generate ester of methanol. Pd^{2+} is a powerful oxidant ($E^0Pd^{2+}/Pd^0 = 0.98$ V vs. NHE), with electronic configuration d^8 and high ionization potential (19.42 eV), and it is characterized as a "soft" metal ion by the Pearson definition. Consistent with these soft properties of Pd^{2+} are the well-known reactions of Pd^{2+} with arenes to produce phenyl-palladium species. Therefore Pd^{2+} allows facile reactions with alkanes ("soft bases") including methane.

The oxidation process was carried out with the use of the apparatus shown in Fig. 1. The autoclave was charged with 100 ml of fuming sulfuric acid with 30% content of free SO_3 and with 0.3 g of palladium in the form of powder (concentration of Pd in oleum, 1.55 wt %). Methane was pressurized in an amount of 0.2 mole (4.5 MPa in 160°C).

Two series of experiments were carried out. In the first one, the temperature was varied within the range 90–180°C for a constant reaction time (2 h). In the second series, the process was carried out over a period from 1 to 20 h at a temperature of 160°C.

The reaction mixture from the autoclave containing the methyl ester of sulfuric acid was subjected to hydrolysis in order to obtain methanol.

RESULTS AND DISCUSSION

The first series of experiments should allow one to establish the process temperature which will be the most advantageous to achieve the largest amounts of methanol. The reaction time was 2 h. The results obtained were shown in Fig. 2.

The presence of carbon dioxide, formaldehyde, and methanol was found. At lower temperatures none of the products was observed. At 90°C formaldehyde was formed in trace amounts. An increase of temperature causes the formation of larger amounts of both methanol and carbon dioxide.

The second series of experiments was performed in order to establish the influence of the process duration on the formation of the desired product that is methanol. The results are presented in Fig. 3. The prolongation of the process time favors the formation of methanol and carbon dioxide, however the largest growth was observed over a period of 1–10 h.

The oxidizing agent in our case was sulfur trioxide, as the acid used was sulfuric acid, whereas the catalyst was metallic palladium. The following reactions proceed in the studied system:

$$CH_4 + SO_3 + H_2SO_4 \longrightarrow CH_3OSO_3H + SO_2 + H_2O, \quad \text{(I)}$$

$$CH_4 + 4SO_3 \longrightarrow CO_2 + 4SO_2 + 2H_2O. \quad \text{(II)}$$

Methanol was produced by hydrolysis of CH_3OSO_3H

$$CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4. \quad \text{(III)}$$

Sulfuric acid is the single largest commodity chemical produced in the world today and is prepared from the oxidation of sulfur dioxide. The technology for the

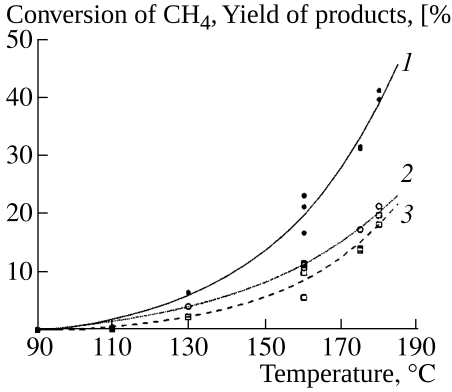

Fig. 2. Influence of the reaction temperature on changes in methane conversion and product yield. Reaction time 2 h, 30% $S0_3$ in oleum, 1.55 wt % Pd in oleum: (*1*) methane conversion, (*2*) carbon dioxide yield, (*3*) methanol yield.

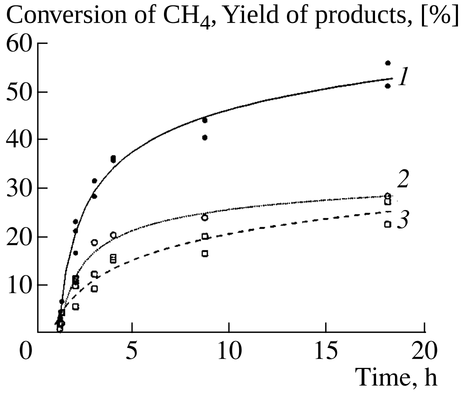

Fig. 3. Effect of residence time on changes in methane conversion and product yield. Reaction temperature 160°C, 30% SO_3 in oleum, 1.55 wt % Pd in oleum: (*1*) methane conversion, (*2*) carbon dioxide yield, (*3*) methanol yield. See keys of Fig. 2.

reoxidation of sulfur dioxide to sulfuric acid (through sulfur trioxide) with air is practiced on a large scale and is relatively inexpensive.

$$SO_2 + 0.5O_2 \longrightarrow SO_3, \tag{IV}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4. \tag{V}$$

Sulfur trioxide and sulfuric acid are the substrates in methane oxidation.

Periana *et al.* [20] noted that the inorganic salts of Tl, Au, Pd, and Pt promoted oxidation of methane in strong oxidizing acids such as concentrated H_2SO_4. Catalyst life as well as reaction selectivities were poor with these metal salts because of irreversible bulk metal formation. Reoxidation of the reduced forms was not possible with suitable oxidants. In our research, palladium in metallic form was used. Oxidation of this form was possible because of a free sulfur trioxide. Pd(0) was oxidized to Pd(II) in the oxidizing environment of sulfuric acid containing SO_3. Pd(II) is a good catalyst in the activation step of the C–H bond [15] since it is both a strong electrophile and a good 2*e* oxidant that allows one to avoid the formation of radicals.

Activation of the C–H bond proceeds as a result of the interaction with the palladium ions. However, it has not been proved whether it is the mechanism of electrophilic substitution or oxidizing addition. It is commonly considered that the activation proceeds according to the mechanism of electrophilic substitution [15, 19, 24, 25]. The complex $Pd^{2+}–CH_3^-$ is formed.

$$Pd^{2+} + CH_4 \rightleftharpoons Pd^{2+}–CH_3^- + H^+. \tag{VI}$$

Subsequently, functionalization takes place, that is, the formation of the monomethyl ester of sulfuric acid as a result of the nucleophilic attack of the bisulfate group.

$$Pd^{2+}–CH_3^- + H_2SO_4 \longrightarrow CH_3SO_4H + Pd + H^+. \tag{VII}$$

Palladium undergoes oxidation due to the action of sulfur trioxide:

$$Pd + SO_3 \longrightarrow Pd^{2+} + SO_2 + O^{2-}. \tag{VIII}$$

Water is formed from oxygen (reaction VIII) and two hydrogen atoms (reactions VI, VII).

The rate of formation of methyl bisulfate during the time is presented in Fig. 4a. It should be adjudicated

Variation of the product and substrate content in the autoclave over time. Reaction temperature 160°C, 30% SO_3 in oleum, 1.55 wt % Pd in oleum

Time, h	Moles, mol				
	CH_4	SO_3	CH_3OSO_3H	CO_2	SO_2
1.17	0.183	0.699	0.005	0.002	0.013
1.17	0.184	0.700	0.004	0.002	0.012
1.27	0.176	0.675	0.009	0.004	0.027
1.27	0.176	0.675	0.009	0.004	0.027
2.00	0.149	0.555	0.019	0.021	0.103
2.00	0.157	0.572	0.011	0.021	0.095
2.00	0.145	0.543	0.022	0.022	0.110
3.00	0.126	0.440	0.025	0.038	0.178
3.00	0.132	0.452	0.019	0.038	0.172
4.00	0.119	0.421	0.031	0.040	0.189
4.00	0.120	0.423	0.030	0.040	0.188
8.75	0.111	0.377	0.032	0.047	0.218
8.75	0.104	0.363	0.039	0.047	0.225
18.25	0.081	0.282	0.053	0.055	0.274
18.25	0.091	0.300	0.044	0.055	0.265

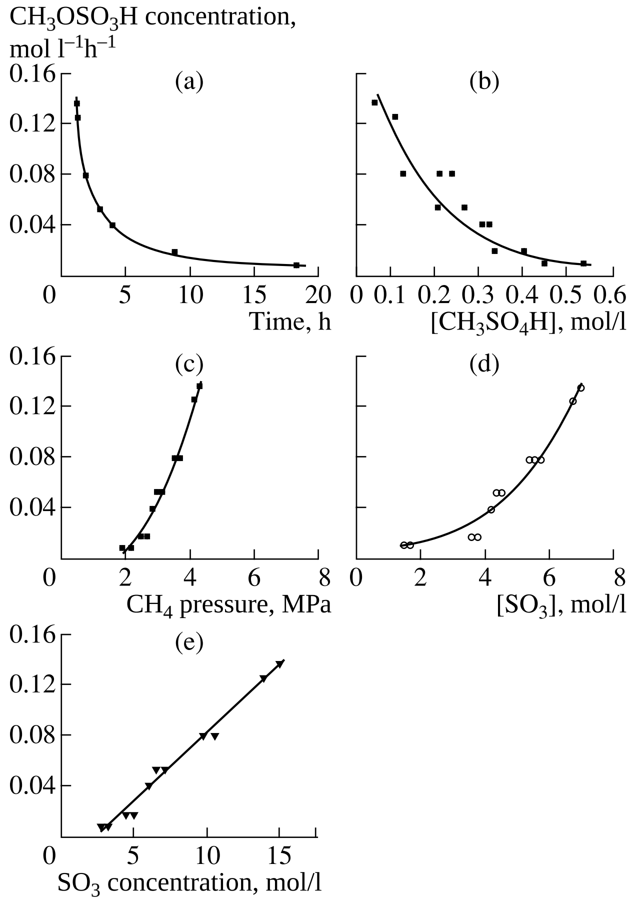

Fig. 4. Variation of the rate of methyl bisulfate formation over time. Reaction temperature 160°C, 30% SO_3 in oleum, 1.55 wt % Pd in oleum.

whether from a technological point of view it would be purposeful to prolong the process running time. This allows one to actually produce larger and larger amounts of the ester; however, the gain in concentration decreases with time.

The rate of formation of methyl bisulfate decreases with increasing methyl bisulfate concentrations (Fig. 4b). This is probably the reason why the rate of the reaction decreases over time. The rate of formation of methyl bisulfate increases with increasing methane partial pressure (Fig. 4c) and with sulfur trioxide concentration (Fig. 4d). Figure 4e shows the relation between the rate of formation of methyl bisulfate and the product of methane partial pressure and sulfur trioxide concentration. The shape of the plot (straight line) proves that the reaction is first order for methane and first order for sulfur trioxide.

Analysis of the course of the curves representing variation of the rate of formation of the methyl bisulfate vs. methyl bisulfate concentrations, methane partial pressure, sulfur trioxide concentration, the product of methane partial pressure and sulfur trioxide concentration, and changes in the number of moles of the substrates and products during the oxidation process of methane (table) allowed us to conclude that the rate of ester formation depends on the partial pressure of methane, the concentration of free sulfur trioxide in sulfuric acid, and the concentration of ester itself in the reaction mixture.

The reaction proceeds most rapidly at a high partial pressure of methane and at a high concentration of sulfur trioxide. An increase of methyl bisulfate concentration in the reaction mixture is the reason for a decline in the rate of its formation. The rate of formation of the methyl bisulfate can be described by equation

$$w_{CH_3SO_4H} = k_1 P_{CH_4}[SO_3] - k_2[CH_3SO_4H],$$

where $w_{CH_3SO_4H}$ is the rate of methyl bisulfate formation [mol/(l h)]; P_{CH_4} is the partial pressure of methane [MPa]; $[SO_3]$ is the concentration of free sulfur trioxide in solution [mol/l]; $[CH_3SO_4H]$ is the concentration of methyl bisulfate in the autoclave [mol/l]; and k_1 [1/(MPa h)], k^2 [1/h] are the reaction rate constants.

The rate constants were determined by Marquardt's method [26]: $k_1 = 0.00464$ MPa^{-1} h^{-1}, $k^2 = 0.05455$ h^{-1}.

CONCLUSIONS

The catalytic Pd-fuming sulfuric acid system allows us to produce methanol from methane at low temperatures. In the first stage of this process, the monomethyl ester of sulfuric acid is produced, while in the second stage methanol is formed as a result of hydrolysis. Both elevated temperatures and prolongation of the reaction time allowed us to produce larger amounts of methanol. The highest increase of the conversion of methane into methanol was observed over a period of 1–20 h. We obtained methanol with a yield of 20% after 10 h and 25% after 18 h at a temperature of 160°C.

The reaction of methyl bisulfate formation proceeds at a high concentration of sulfur trioxide and at a high partial pressure of methane. The increase of ester concentration in the reaction mixture is the factor that inhibits the formation of the ester.

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