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Catalytic system containing metallic palladium in the process of methane partial oxidation

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Abstract

The oxidation of methane to organic oxygenates over metallic palladium dissolved in oleum was studied. Methanol was obtained by the transformation of methane into methyl bisulfate and dimethyl sulfate. Subsequently, methanol was formed as a result of ester hydrolysis. The reaction conditions were temperature 160 °C, pressure of methane 3.5 MPa, time 2 h, content of sulfur trioxide in fuming sulfuric acid 30%. Palladium can be recovered and used many times without reduction in the process yield. The byproducts formed in the process may be reclaimed and reused.

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Keywords: Methane; Partial oxidation of methane; Methanol; Palladium; Oleum; Methyl bisulfate; Dimethyl sulfate

1. Introduction

The reserves of global natural gas have doubled over the past 20 years. Gas reserve estimates have grown particularly rapidly in the former Soviet Union and in the developing countries in the Middle East, South and Central America, and the Asia–Pacific region. For January 1, 2001, the confirmed world gas reserves were estimated at 5278 trillion cubic feet (149.37 Tm^3) [1]. Most of the known world natural gas reserves are inconveniently located in remote and thinly populated areas. The lack of infrastructure is the major barrier to increased worldwide gas consumption. Most of the gas is currently sent by pipeline, which calls for proximity to the target areas and the possibility of laying pipelines over reasonable terrain. Another transportation option is liquefied natural gas (LNG), which needs a liquefaction plant. Both methods are expensive and potentially hazardous. Natural gas resources are not fully utilized, mainly due to the transportation costs. This situation could be changed by the development of a simple and inexpensive method of conversion of methane into oxygenated derivatives, which have proved to be easily transportable liquid products.

Selective oxidation of methane to methanol or other oxygenates is one of the problems unsolved up to now. The achievement of this goal is, however, not a straightforward task. The C–H bond in the methane molecule is very strong (438.8 kJ/mol). The reaction conditions which allow cleavage of this bond and oxidation of methane are simultaneously favorable for the oxidation of methanol to formaldehyde and to carbon dioxide, while the energy of the C–H bond in methanol amounts to 373.5 kJ/mol.

Although studies of methane oxidation to its oxygenated derivatives with solid catalysts and under elevated pressure have been carried out worldwide for several years, the results are not satisfactory. Methane oxidation is usually carried out at high temperatures of 400–700 °C. The desired products are obtained as a result of free-radical reactions with a yield of several percent [2]. In the radical processes, methanol and other oxygenates are significantly more reactive than methane.

This problem can be bypassed by finding a different reaction system whereby methane becomes more reactive than its products. Gol'dshleger was the first who carried out studies concerning the oxidation of alkanes to alcohols by of platinum complexes in water [3],

$$\begin{aligned}&2\mathrm{CH_4} + [\mathrm{PtCl_6}]^{2-} + \mathrm{H_2O} + 2\mathrm{Cl}^-\\&\quad\overset{[\mathrm{PtCl_4}]^{2-}}{\rightarrow}\ \mathrm{CH_3OH} + \mathrm{CH_3Cl} + [\mathrm{PtCl_4}]^{2-} + 3\mathrm{HCl}.\end{aligned}$$

In recent years some methane oxidation reactions that utilize electrophilic late transition metals in strongly acid media

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have been discovered. The reaction of methane and acid leads to the methyl ester, which does not readily undergo oxidation. Subsequently, as a result of ester hydrolysis, methanol is formed:

$$\text{methane} + \text{oxidant} + \text{acid} \rightarrow \text{methyl ester of acid} + \text{reduced oxidant},$$

$$\text{methyl ester of acid} + \text{water} \rightarrow \text{methanol} + \text{acid}.$$

Such a process is currently of immense interest. The objective of the studies is the selection of a catalyst for the first reaction, as well as an acid and an oxidizer. Periana et al. [4] claim that the catalyst may be one or more metals from group B of the periodic system, which readily undergo two-electron reduction, but hardly undergo one-electron reduction. The acids recommended by these investigations include HNO_3, H_2SO_4, CF_3SO_3H, H_3PO_4, H_2SeO_4, HBr, HCl, heteropolyacids, and anhydrides or salts of the acids $H_4P_2O_7$ and $H_2S_2O_7$. An oxidizing agent may be O_2, H_2SO_4, SO_3, HNO_3, and H_2SeO_4.

The systems mercury(II) bisulfate–sulfuric acid [5–7] and bis(2,2′-bipirimidine)Pt(II)Cl_2–fuming sulfuric acid [7–10] have been of particular interest.

In the case of the catalytic system containing mercury in the form of bisulfate dissolved in sulfuric acid [5–7], the mercury ions catalyze the methane oxidation by sulfuric acid to methyl bisulfate, water, and sulfur dioxide. The authors are of the opinion that in such a reaction methyl bisulfate can be obtained with a selectivity of 85% at a methane conversion of 50%. The methyl bisulfate is subsequently subjected to hydrolysis, as a result of which methanol is formed.

Bis(2,2′-bipirimidine)Pt(II)Cl_2–fuming sulfuric acid [7–10] has turned out to be the best catalytic system. Periana et al. [10] achieved a 90% conversion of methane at a selectivity of 81% to methyl bisulfate.

Taylor et al. [11], Sen and co-workers [12,13], and Vargaftik et al. [14] have studied catalytic systems containing metals such as Mn, Fe, Co, Cu, Pb, and Pd, together with fluoroacetic acid. As a result of the reaction with methane, methyl fluoroacetate, which can be subsequently transformed into methanol, was obtained. The best catalytic system in this investigation was palladium acetate–fluoroacetic acid [11,12].

Other examples for such a type of catalytic system are mercury, cerium, or palladium sulfates in sulfuric acid [15], mercury and palladium sulfates in fuming sulfuric acid [16], peroxytrifluoroacetic acid–palladium [17], and $EuCl_3$–Zn–CF_3CO_2H [18,19].

Our studies related to the catalytic system palladium–fuming sulfuric acid for methane-to-methanol conversion. Palladium in the metallic form, as well as palladium sulfate, was used. The aim was to prove that metallic palladium can be used in the catalytic system for the methane conversion process and that the form of Pd can be used optionally.

2. Experimental

2.1. Catalyst

In the studies concerning methane conversion to methanol, Pd–oleum, $PdSO_4$–oleum, Pd–H_2SO_4, $PdSO_4$–H_2SO_4 catalytic systems were used. The following reagents were used: powdered Pd (Merck), $PdSO_4$ (Merck), oleum–30 wt% SO_3 (Merck), H_2SO_4 (POCh).

2.2. X-ray diffraction

We used X-ray diffraction to characterize the catalyst after the reaction. The powder X-ray diffraction measurements were carried out on an HZG-4 diffractometer using Co-K_α radiation. The X-ray tube was operated at 30 kV and 35 mA. The 2θ angle was scanned at a rate of 0.05°.

2.3. Product identification

The identification of the reaction products was achieved using natural abundance ^{13}C NMR measurements performed on a Bruker DPX 400 spectrometer, equipped with a 5-mm ^{1}H/BB–inverse probehead, operating at 100.62 MHz, using 20,480–25,600 transients, spectral width 31,850 Hz, acquisition time 1.03 s, delay time 1 s, and digital resolution 0.97 Hz per point. DMSO-d_6 was used as external lock and reference. All measurements were performed with a 5-mm coaxial tube.

The products were quantified by gas chromatography (Fisons). Separation of the components HCHO, CH_3OH, CO_2, and H_2O was achieved using a Porapak T-packed column. CH_4, N_2, and CO were separated by a molecular sieve 5A packed column. The effluent of both columns was connected to a TCD.

2.4. Reactions

The oxidation process was carried out in an autoclave (Berghof 200) equipped with a magnetic stirrer, charged with 100 ml of acid and with a solid catalyst. Methane was pressurized up to 3.5 MPa from a gas cylinder equipped with a reduction valve. The temperature of the reaction mixture was measured by a thermocouple connected with a temperature controller. The reaction temperature was 160 °C. After 2 h the reactor was cooled with water to 20 °C. The gaseous reaction products were sampled through a septum for gas chromatography analysis. The reaction products were monitored by recording of ^{13}C NMR spectra of the crude liquid reaction mixtures.

The reaction mixture (ca. 100 ml) was subjected to hydrolysis in distilled water by dropping it very slowly into the water while maintaining a temperature no higher than 40 °C in order to avoid the evaporation of methanol.

Subsequently 50 ml of post-hydrolytic liquid was subjected to slow distillation. The distillate was analyzed with a gas chromatograph to determine the content of methanol and formaldehyde.

3. Results

Methanol and trace amounts of formaldehyde were obtained in the systems $PdSO_4$–H_2SO_4, Pd–oleum, and $PdSO_4$–oleum.

After the methane esterification the reaction mixture was analyzed by ^{13}C NMR spectroscopy. In all samples the main product gave an intensive signal at 60.8 ppm in the ^{13}C NMR spectrum. This intense signal coexisted with a very small signal at 65.7 ppm and with a small signal at 91.0 ppm. After a longer time palladium was precipitated, the signal at 91.0 ppm disappeared completely, and the formation of a metallic mirror was observed. Fig. 1 presents an example of the spectrum which contained the three NMR signals. Considering the difficulties in the interpretation of the NMR spectra measured in fuming sulfuric acid due to its high acidity and reactivity [20], the signals were assigned and the reaction products were identified by comparison of the analyzed spectra with the spectra of reference samples. Thus, we performed ^{13}C NMR spectra of mixtures of fuming sulfuric acid with ca. 5% addition of methanol, dimethyl sulfate, formaldehyde, formaldehyde dimethylacetal, methyl formate, trimethyl orthoformate, and formic acid. The resulting ^{13}C NMR signals are summarized in Table 1.

The addition of methanol to sulfuric acid results in the formation of methyl hydrogen sulfate (reaction (1)), (Table 1, item 2):

$$H_2SO_4 + CH_3OH \rightleftarrows CH_3OSO_3H + H_2O. \qquad (1)$$

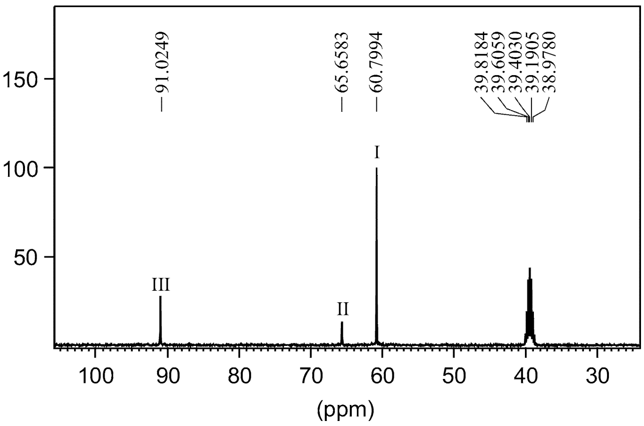

Fig. 1. ^{13}C NMR spectrum of the crude reaction mixture from the autoclave after 2 h at 160 °C, methane pressure 3.5 MPa, 0.2 g Pd in 100 ml oleum. (**I**) CH_3OSO_3H, (**II**) $(CH_3O)_2SO_2$, (**III**) $H_2C(OSO_3H)_2$.

Table 1
The ^{13}C NMR signals of the measured mixtures

Item	Measured mixture	Observed signals (ppm)
1	Crude sample (Fig. 2)	60.8; 65.7; 91.0
2	$H_2SO_4 + CH_3OH$	60.7[a]
3	$H_2SO_4 + (CH_3O)_2SO_2$	60.6; 62.0[b]
4	$H_2SO_4 + HC(OCH_3)_3$	61.4[c]
5	$H_2SO_4 + HCOOCH_3$	61.2[c]
6	$H_2SO_4 + H_2C(OCH_3)_2$	61.8; 91.3
7	$H_2SO_4 + HCHO$	91.0
8	$H_2SO_4 + HCOOH$	No signal[c]

[a] In the ^{13}C NMR spectra of the mixture of methanol with 95% H_2SO_4 the signal at 58.1 ppm was observed.

[b] In the ^{13}C NMR spectra of the mixture of dimethyl sulfate with 95% H_2SO_4 the signal at 58.0 ppm (major) and 59.6 ppm (minor) was observed.

[c] The spectrum was recorded when gas (CO) was completely evacuated.

Based on the above analyses it can be concluded that the main signal (60.8 ppm) represents sulfuric acid monomethyl ester CH_3OSO_3H (**I**), which is the predominant product of the reaction mixture. The same resonance position for methyl hydrogen sulfate was also mentioned in the literature [5]. Determining the contaminated product, responsible for the presence of the signal at 65.7 ppm (Fig. 1, Table 1, item 1) is not quite incontrovertible. However, since the mixture of fuming sulfuric acid with methanol gave a signal at 60.7 ppm (Table 1, item 2) and the mixture of fuming sulfuric acid with dimethyl sulfate gave two signals (major at 62.0 ppm and minor at 60.6 ppm) (Table 1, item 3), the signal at 62.0 ppm in the later case could be attributed to dimethyl sulfate. Based on the above experimental observation and taking into account the dependence of the chemical shift in the ^{13}C NMR spectra of the compounds measured in sulfuric acid media on concentration, acidity, and SO_3 content, causing a slight shift in resonance positions (Table 1, item 2 and note a, item 3 and note b), the signal at 65.7 ppm of contaminated product of a crude sample (Table 1, item 1) could be assigned to dimethyl sulfate. These products indicated that methanol was the main product of the oxidation of methane. A further analysis was conducted as follows. The addition of trimethyl orthoformate (Table 1, item 4) or methyl formate (Table 1, item 5) to fuming sulfuric acid caused the evolution of gas. The ^{13}C NMR spectrum exhibited a signal at ca. 61 ppm. In the ^{13}C NMR spectrum of the mixture of fuming sulfuric acid and formaldehyde dimethyl acetal (Table 1, item 6), apart from a signal at 61.8 ppm, a signal at 91.3 ppm was observed. The latter signal was also observed for the mixture of formaldehyde and sulfuric acid (Table 1, item 7) and in the spectrum of a sample taken from the autoclave. These observations led to a conclusion that sulfuric acid caused an exchange of methoxy groups, yielding methyl hydrogen sulfate (**I**):

$$H_2SO_4 + HCOOCH_3 \rightarrow CO + CH_3OSO_3H + H_2O, \qquad (2)$$

$$3H_2SO_4 + HC(OCH_3)_3 \rightarrow CO + 3CH_3OSO_3H + 2H_2O, \qquad (3)$$

$$2H_2SO_4 + 2SO_3 + H_2C(OCH_3)_2 \rightleftarrows H_2C(OSO_3H)_2 + 2CH_3OSO_3H. \qquad (4)$$

In the case of the reaction mixture of formaldehyde, dimethyl acetal, and/or formaldehyde and sulfuric acid, the formation of sulfuric acid monosulfooxymethyl ester $H_2C(OSO_3H)_2$ (**III**) could be postulated:

$$2H_2SO_4 + HCHO \rightleftarrows H_2C(OSO_3H)_2 + H_2O. \tag{5}$$

In our opinion compound **III** is responsible for the signal at ca. 91 ppm and indicative of formaldehyde as a byproduct of the oxidation of methane. The disappearance of the signal at 91.0 ppm after a longer time at atmospheric pressure is the result of the subsequent oxidation of formaldehyde or **III** leading to formic acid, which is unstable in sulfuric acid and decomposes to CO and H_2O.

The GC analysis indicated that carbon dioxide was the only gaseous product after methane oxidation. The following reactions proceeded in the autoclave:

$$CH_4 + SO_3 + H_2SO_4 \rightarrow CH_3OSO_3H + SO_2 + H_2O, \tag{6}$$

$$2CH_4 + 2SO_3 + H_2SO_4 \rightarrow CH_3OSO_3CH_3 + 2SO_2 + 2H_2O, \tag{7}$$

$$CH_4 + 2SO_3 + 2H_2SO_4 \rightarrow CH_2(OSO_3H)_2 + 2SO_2 + 2H_2O, \tag{8}$$

$$CH_4 + 4SO_3 \rightarrow CO_2 + 4SO_2 + 2H_2O. \tag{9}$$

In order to prepare methanol from esters, the reaction mixture should be subjected to hydrolysis according to the reactions

$$CH_3OSO_3CH_3 + H_2O \rightarrow CH_3OSO_3H + CH_3OH, \tag{10}$$

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4. \tag{11}$$

After hydrolysis, esters were not detected by ^{13}C NMR spectroscopy. The reaction mixture contained methanol, water, sulfuric acid, and traces of formaldehyde. Formaldehyde is produced according to the equation

$$H_2C(OSO_3H)_2 + H_2O \rightleftarrows 2H_2SO_4 + HCHO \tag{5a}$$

which is the opposite of Eq. (5). Formaldehyde is an unstable product in sulfuric acid. It may be oxidized to carbon oxide and water through formic acid:

$$HCHO \overset{H_2SO_4}{\rightarrow} (HCOOH) \overset{H_2SO_4}{\rightarrow} CO + H_2O. \tag{12}$$

The effect of increasing the content of palladium in the reaction mixture on the formation of methanol is shown in Fig. 2. Palladium was used both in the metallic form and as palladium sulfate. It can be seen that only the metal content in the reaction mixture is significant, whereas the form in which it was introduced was not important. The largest yield enhancement was observed up to 0.2 g palladium in 100 ml oleum. A further increase of the catalyst amount results in small increases of the ester amount. Solubility of palladium in oleum is limited. That is why a further increase of the catalyst amount in acid does not much influence the ester yield. The mass of metallic palladium recommended is in the range 0.1–0.2 g or 0.22–0.45 g palladium sulfate in 193.5 g fuming sulfuric acid. The presence of metallic palladium in the reaction mixture was not determined when the amount of palladium used at the start was smaller than 0.2 g. Palladium which did not undergo dissolution was identified by XRD (Fig. 3) and maintained for reuse. In the experiments with the recycled catalyst we did not observe a difference in the yield of the methanol formation or in the methane conversion in relation to the experiments in which "fresh" palladium was used.

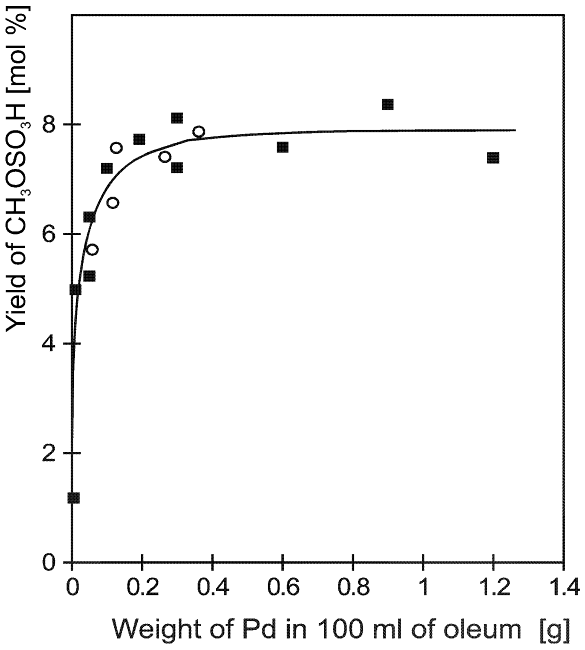

Fig. 2. The effect of the palladium content on the yield of methanol. The reaction conditions: 160 °C, pressure of methane 3.5 MPa, time 2 h, content of sulfur trioxide in fuming sulfuric acid 30%, catalyst in the form (■) Pd metallic, (○) $PdSO_4$.

Palladium which underwent dissolution was also recovered. We have observed that metallic palladium precipitated 24 h after the hydrolysis has been accomplished. In this way 70 to 80% of the metal was recovered depending on the type of experiment. Recovered palladium was not different from

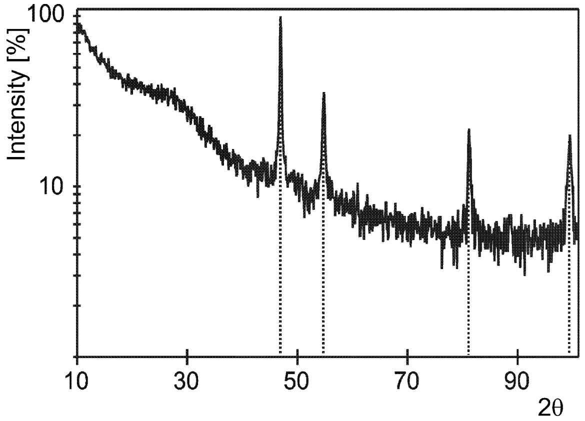

Fig. 3. X-ray diffractogram. Vertical dashed line—Pd reflections by JCPDS No. 5-681.

that one used in the reaction, as was confirmed by XRD. The reuse of the metal as a catalyst influences neither the yield of methanol formation nor the methane conversion. The same palladium was recovered and used repeatedly as a catalyst in the methane oxidation process. The ester was obtained with the same yield even after 10 times. Thus the multiple utilization of the same catalyst in successive syntheses is possible. One can ascertain that this catalytic system is long-lived and does not deactivate with time. This is particularly worth emphasizing on account of the high price of palladium.

Fuming sulfuric acid with various contents of free SO_3 has been used in our studies. A decrease in the content of sulfur trioxide in sulfuric acid leads to a reduction of both the degree of methane conversion (Fig. 4) and the yields of the ester and carbon dioxide. The increase in the content of free sulfur trioxide causes an increase in the selectivity of methane oxidation to carbon dioxide and a decline in the selectivity to methanol. When the reaction medium did not contain free SO_3, the methane conversion did not proceed over metallic Pd.

The application of $PdSO_4$ and sulfuric acid permitted the formation of the ester with a yield of about 80% when calculated on the basis of palladium, that is, with a 1.1% yield in relation to methane. The ester was the only product. The final reaction mixture contained palladium in the metallic form. The presence of palladium in such a form was confirmed by XRD. The precipitated metal comprised 80 mol% of the palladium used in the sulfate form.

The yield of the oxidation of methane to the ester in relation to palladium amounted to 4700% (160 °C, 3.5 MPa, 2 h, 30 wt% SO_3 in oleum, 0.005–2 g Pd) when the catalytic system contained fuming sulfuric acid. This confirms the catalytic properties of metallic palladium as well as the occurrence of multiple reoxidation of palladium.

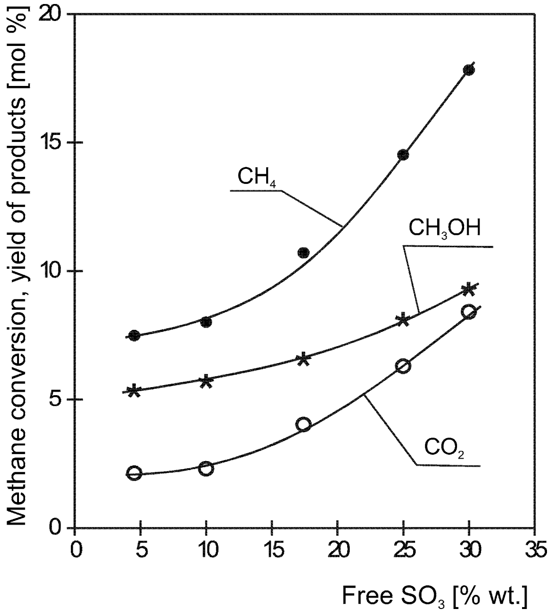

Fig. 4. The effect of the free SO_3 in oleum content on the methane conversion and yield of the products. The reaction conditions: 160 °C, pressure of methane 3.5 MPa, time 2 h, 0.1 g Pd in 100 ml oleum.

In every experiment a mass balance of methane has been accomplished. The differences between the mass of carbon (originating of course from methane) before the reaction and the mass of coal products after the reaction were not large (from 1 to 8%).

4. Discussion

Until now palladium has been applied as palladium sulfate with oleum [16] or as palladium acetate [11,12] with trifuoroacetic acid. The catalytic system Pd(0)–fuming sulfuric acid proposed by us, where palladium occurs in the form of palladium powder dissolved in fuming sulfuric acid, has not been described until now. There is a great difference between using palladium(0) powder, utilized by us, and palladium(II) sulfate, used by Basickes et al. [16]. Pd(II) is a good $2e^-$ oxidant but Pd(0) is not. It is worth noting that Periana at al. [10] mentioned palladium as one of the metals which was used in combination with sulfuric acid, but the catalyst life as well as the reaction selectivities were poor because of irreversible bulk-metal, i.e., Pd(0) formation that occurs with the use of noble metals. Palladium is not soluble in sulfuric acid even after heating. We were able to dissolve palladium in hot fuming sulfuric acid. Fuming sulfuric acid containing free sulfur trioxide is a stronger oxidant than sulfuric acid. As a result of the reaction of Pd(0) with sulfur trioxide, palladium is oxidized to Pd(II); therefore it may be used in any form. Fig. 5 presents the consecutive stages of the oxidation and reduction to which palladium was subjected during the methane conversion to methyl bisulfate. The catalytic process relies on the formation of the unstable metalloorganic complex Pd^{2+}–CH_3^-, which reacts with sulfuric acid. The carbon atom undergoes oxidation to methyl bisulfate while palladium is reduced to Pd(0). The sulfuric trioxide present in the reaction mixture causes the reoxidation of Pd(0) to Pd(II). As a result of the reaction of O^{2-} (product of stage 1) with two H^+ (products of stages 2 and 3), water is formed.

The methane conversion could not proceed in the case of metallic Pd without free SO_3 because the first stage of the catalytic process will not take place.

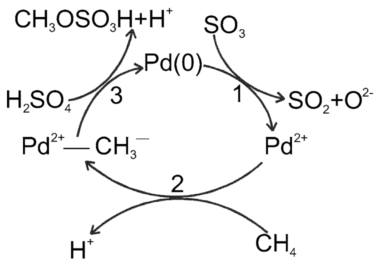

Fig. 5. Redox transformation of palladium.

When $PdSO_4$ and sulfuric acid were used as catalysts the conversion of methane proceeded up to the moment when the oxidized form of palladium was used up. Palladium reoxidation could not take place due to the lack of sulfur trioxide. There was no carbon dioxide in the product because reaction (9) did not proceed due to the absence of sulfur trioxide.

Sulfur dioxide formed in reactions (6)–(9) can be oxidized to sulfur trioxide, which is a substrate in these reactions:

$$SO_2 + 0.5O_2 \rightarrow SO_3. \tag{13}$$

By combining the reactions proceeding in the process of methane conversion to methanol reactions, (6), (7), (10), (11), and (13), we obtain

$$CH_4 + 0.5O_2 \rightarrow CH_3OH. \tag{14}$$

In an ideal situation, methanol would be formed with a yield amounting to 100%, and the only substrates consumed in this process would be methane and oxygen. Sulfur trioxide would only perform the role of the reagent which transports oxygen. Taking into consideration that carbon dioxide is produced in the parallel reaction along with ester, as well as that much more water is consumed in the hydrolysis than would result from the oxidation stoichiometry, the supply of additional amounts of sulfur trioxide is necessary. After the distillation of methanol and significant amounts of water from the reaction mixture, sulfuric acid in a concentration of ca. 80–90% was obtained. This acid can be reused after saturation by sulfuric trioxide or utilized in various ways, for example, in the fertilizer industry.

5. Conclusions

We report the development of a new catalytic system, Pd–oleum, for the oxidation of methane to methyl ester. We have demonstrated that palladium in the metallic form can be used. The mass of metallic palladium recommended is in the range 0.1–0.2 g in 100 ml of fuming sulfuric acid (0.05–0.10 wt%). Sulfur trioxide is necessary for the appropriate function of the catalytic palladium system. The byproducts formed in the process may be reclaimed and reused. Palladium can be recovered and used many times without a reduction in the process yield. The diluted sulfuric acid may also be recycled after the concentration of sulfuric acid.

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