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REACTOR OF CATALYTIC METHANE OXIDATION FROM VENTILATION AIR — FROM LABORATORY TO QUARTER-TECHNICAL SCALE PROTOTYPE

1. Introduction

The most research efforts in heterogeneous catalysis are directed at understanding the correlations between the catalytic activity of studied contact and its physical-structural properties. One way to address this issue is through examination of specific reaction mechanism which has been of particular interest to many researchers. The most important from these basic studies focus on the effect of variables such as temperature and/or concentration of substrate or product on the reaction rate

In many cases, significant differences in mechanisms may lead to similar microscopic observations, and thus, to similar expressions for the reaction rate. This means that the experimentally determined kinetic parameters usually do not allow firm conclusions on microkinetic mechanism. This problem is especially important for multi-step processes such as the transformation reactions of hydrocarbons, in particular catalytic oxidation. However, it should be noted that any proposed mechanism must be compatible with the evaluated kinetics.

Despite the significant development of noble and transition metals surface chemistry, various crucial aspects of metal catalysis have not yet been fully explained. This is due to the apparent complexity of the phenomena involving a number of factors i.e., dynamic character of the surface of dispersed metal particles, which can be reconstructed under catalytic conditions, and its susceptibility to carbonation especially in reactions with hydrocarbon reactants. The role of carbon deposits is still not sufficiently well understood. There is also

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lack of systematized knowledge about thermal stability of mentioned systems and correlations between activity, selectivity and physicochemical, oxidation-reductive properties.

One aim of this research was to define the methane oxidation rate dependence on temperature and partial pressure of substrates at low methane concentration in reaction mixture and with complete elimination of the influence of external diffusion on kinetic results. These experiments give us the opportunity to evaluate correctly the real activity of different catalyst and also the reaction order with respect to methane. Furthermore, using the obtained data make it possible to determine the process rate for larger than the laboratory scale.

2. Investigation methodology

Alumina supported palladium catalysts were tested for methane oxidation. Physicochemical properties of these systems are described in detail elsewhere [3, 5–10]. All kinetic experiments were performed in a gradientless reactor, as described previously in papers 1 and 2. Gases; hydrogen, methane, oxygen and helium (Praxair, Poland) were fed into the reactor device equipped with mass flow BETA-ERG controllers and power supplies of the same manufacturer.

Flow controllers were carefully calibrated. The temperature of the reactor was regulated by Trol-8120 controller connected with chromel-alumel thermocouple placed directly in the catalyst bed. The rate of process, expressed as TOF (turnover frequency) was calculated from measurements of the conversion degree, according to the equation valid for gradientless reactors [1, 2].

$$r = F (C_{we} - C_{wy}) / (W \cdot (2 V_{H_2} / V_M)) \quad (1)$$

where:

- r — reaction rate, s⁻¹,
- W — catalyst sample weight used to measure, g,
- F — CH₄ volumetric flow through the reactor, mol/s,
- C_{we}, C_{wy} — input and output concentrations of CH₄, —,
- V_{H_2} — volume of hydrogen chemisorbed by the sample, cm³/g,
- V_M — molar volume of hydrogen, 22 414 cm³/mol.

The dependence of the reaction rate on the conversion degree was determined in isothermal experiment (773 K) as a function of both the conversion of methane and its partial pressure. The reaction mixture was composed of air, methane, oxygen, helium (instead of nitrogen) to simulate the composition of air. The analysis of products was performed at the temperature of 305 K using Chrompack CP 9001 gas chromatography unit equipped with a capillary column Chrompack Pora Bond (with 50 m length) operated with helium as a carrier gas. The system proved a very high sensitivity and separation quality for the reaction mixture (helium ballast

from the reaction gases was not analyzed). Analyses were performed at the temperature of 305 K, using a PC as an integrator.

Industrial-scale researches were conducted at the Wrocław University of Technology on installation that allows effective testing of large ceramic fillings (5 kg, 4,7 dm³) [5].

Physicochemical properties of palladium catalysts were studied in the Analytical Laboratory of the Faculty of Chemistry UMCS in Lublin. Palladium contents in the catalysts were determined by X-ray fluorescence. The total surface area of the samples was calculated from performed nitrogen adsorption in a static volumetric apparatus, providing a vacuum not worse than 10⁻⁵ Tr. Metal surface areas of contacts were measured by hydrogen chemisorption performed under conditions described previously in the literature [3, 4].

3. Results of researches

The studied reaction can be described with the following equations:

$$r = k \cdot f(C) \quad (2)$$

$$r = A_0 \cdot e^{-E_a/RT} \cdot p_{\text{CH}_4} \quad (3)$$

$$k = A_0 \cdot e^{-E_a/RT} \quad (4)$$

$$\ln(k) = \ln A_0 - E_a/RT \quad (5)$$

where:

- r — the reaction rate,
- k — the reaction rate constant,
- A_0 — the pre-exponential factor,
- R — the universal gas constant,
- T — the temperature,
- E_a — the activation energy.

The study of methane oxidation in the kinetic reactions have been described in papers [3, 4] and led to the designation of empirical kinetic equation of the process. Experimental and kinetic reaction modeling studies of methane oxidation described elsewhere [3, 4] have been used to propose an empirical kinetic equation for the process. Determined values of the activation energy, the reaction rate and the pre-exponential factor for catalysts with different sizes of palladium crystallites (from 4.7 to over 13.0 nm) are shown in Table 1.

Palladium crystallites size of the catalyst prepared on industrial carrier, and used in the large-scale testing, was included in the range of 7–10 nm. Hence, the parameters of the large-scale reactor were calculated based on the reaction rate constant $k = 0.2035$ for palladium catalyst with crystallites size of 9.6 nm.

TABLE 1

The values of activation energy, reaction rate constant and pre-exponential factor for palladium catalysts

Palladium crystallites size on the catalyst surface, nm	E_a , kJ/mol	Reaction rate constant, k	Pre-exponential factor, A_0
4.7	74.84	0.2211	142269
5.5	62.85	0.4279	32308
6.6	97.03	0.1473	4998678
9.6	80.66	0.2035	370496
13.0	76.19	0.2926	239700

Theoretically calculated gas temperature distribution along the catalyst bed in the reactor was compared with experimental data obtained from a large-scale laboratory reaction. Figure 1 depicts gases temperature distribution along the catalyst bed for two cases (a), with the methane concentration of 1.50% in the air, the reaction gases flow of 20 m³/h and methane conversion of $x = 90\%$, and (b) for methane concentration of 1.30% in the air, the reaction gases flow of 25 m³/h with 90% conversion of methane.

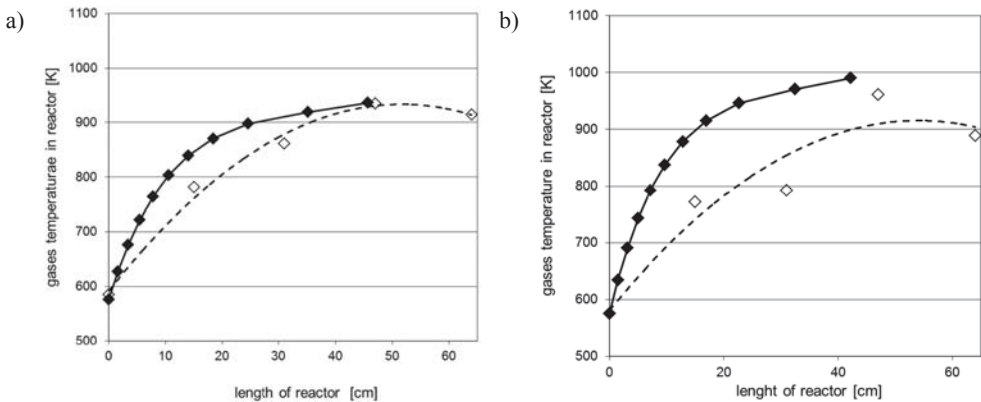


Fig. 1. Gases temperature distribution along the catalyst bed (continuous curve — theoretical calculations, dashed curve — the actual temperature measurement): a) methane concentration of 1.50% in the air, the flow of reaction gases of 20 m³/h and conversion of methane $x = 90\%$; b) methane conversion of 1.30% in the air, the flow of reaction gases of 25 m³/h and methane conversion of $x = 90\%$

The calculations did not include refer to the heat losses associated with the construction of the reactor. Hence, the theoretical values are slightly higher than the experimental ones.

TABLE 2
 The theoretical values of temperature (t , K) and the length of the reactor (l , cm) necessary to achieve the X [-] degree of methane oxidation.
 The assumed reactor diameter is 660 mm

C_{CH_4}	0,75%		1,00%		1,25%		1,50%	
	l , cm	t , K	l , cm	t , K	l , cm	t , °C	l , cm	t , °C
0.00	0.0	603	0.0	603	0.0	603	0.0	603
0.10	2.4	633	3.1	643	3.9	653	4.7	662
0.20	5.0	661	6.7	680	8.3	699	10.0	719
0.30	8.0	687	10.6	715	13.3	743	15.9	771
0.40	11.4	712	15.2	748	19.0	784	22.8	820
0.50	15.5	734	20.7	778	25.8	822	31.0	865
0.60	20.5	755	27.3	805	34.1	856	41.0	906
0.70	26.9	773	35.9	830	44.9	886	53.8	943
0.80	36.0	789	48.0	850	60.0	912	72.0	974
0.90	51.5	801	68.6	867	85.8	933	102.9	998
0.95	67.0	811	89.3	606.9	111.6	949	133.9	1027

Despite only a few positions for temperature measurement distributed inside the large-scale reactor, the expected length of the reactor for achieving methane conversion of 90% does practically overlap with temperature maximum in the large-scale reactor. The further temperature drop is caused by the completion of the reaction at the rear end of the catalyst bed due to the consumption of substrates i. e. methane in the flue gases.

Using all the above information, it is possible to predict dependence of required length of the reactor on the amount of methane, which should be converted in a larger gas stream. The results of calculations for the stream of 3000 m³/h with different methane content are shown in Table 2. For the flow of mentioned stream of gases through the reactor with a diameter of 660 mm, assuming 95% methane conversion, the required bed lengths are as follows:

- 670 mm for the mixture containing 0.75% of methane,
- 893 mm for the mixture containing 1.00% of methane,
- 1116 mm for the mixture containing 1.25% of methane,
- 1339 mm for the mixture containing 1.50% of methane.

The table also shows the theoretical values of temperature of exhaust gases with assumed flow of 3000 m³/h and the temperature of gases entering the reactor (603 K).

4. Conclusions

The comparison of results obtained in a laboratory scale with theoretically calculated values reveals that the resulting kinetic equation is adequate to describe methane oxidation over palladium catalysts with crystallites size in the of 6–10 nm and with methane conversion from 1 to 95% and methane concentration in the air from 0.75 to 1.60%.

Moreover, the obtained data permitted to calculate the heat generated in the catalyst bed, the gas-lift heat and also to design a larger, target reactor for catalytic process of methane oxidation. The data summarized in table 2 show that the appropriate concentration of methane in the reaction gases enable not only the autothermal reactor operation, but also receiving the additional large thermal power, which allows for industrial and economically efficient exploit of mine ventilation air methane.

REFERENCES

- [1] *Nazimek D., Ryczkowski J.*: A Gradientless Reactor for Kinetic Studies of Catalytic Processes (construction of gradientless reactor), *Adsorption Sci. & Technol.* 17, 1999, 805.
- [2] *Nazimek D., Kuśmierz M., Kirszensztejn P.*: Ideal continuous stirred thermobalance reactor, *P. J. of Applied Chem.* 50, 2006, 41.
- [3] *Stasińska B., Marcewicz-Kuba A., Kuśmierz M., Nazimek D., Pańczyk M., Gac W.*: W. Zawadzki, Zadanie 2.1. „Opracowanie założeń technologicznych i optymalnych wypełnień katalitycznych do badań w wielkolaboratoryjnym reaktorze dla katalitycznego utleniania metanu KRUM-1/1”, 2009 (dane niepublikowane).
- [4] *Bot I.*: praca magisterska pt. „Badania kinetyki katalitycznej reakcji utleniania metanu na katalizatorach palladowych”, UMCS, Lublin 2008.

- [5] *Stasińska B., Marcewicz-Kuba A., Kuśmierz M., Nazimek D., Pańczyk M., Gac W.*: W. Zawadzki, Zadanie 2.1. Materiały sprawozdawcze — spotkanie konsorcjum 28.10.2010 r. Zespół UMCS w Lublinie, Lublin 2010.
- [6] *Stasińska B., Machocki A., Antoniak K., Rotko M., Jose L.*: Figueiredo, Filomena Gonçalves,: Importance of palladium dispersion in Pd/Al₂O₃ catalysts for complete oxidation of humid low-methane air mixtures — *Catalysis Today* 137, (2–4), 2008, 329–334.
- [7] *Machocki A., Rotko M., Stasińska B.*: SSITKA studies of the catalytic flameless combustion of methane, *Catalysis Today* 137, (2–4), 2008, 312–317.
- [8] *Stasińska B., Machocki A.*: Influence of carbon dioxide on catalytic combustion of methane, *Polish Journal of Environmental Studies*, 15, No. 6A (2006) 157–160.
- [9] *Machocki A., Stasińska B., Gac W.*: Why does the activity of Pd/Al₂O₃ catalysts depend on the dispersion of palladium phase?, *Polish Journal of Chemical Technology*, 8 (2006) 93.
- [10] *Machocki A., Stasińska B., Gac W.*: Alumina supported palladium catalysts with varied metal dispersion for complete oxidation of methane, *Catalytic Combustion*, P. Forzatti, G. Groppi, P. Ciambelli, D. Sannino (Eds.), Polipress, Milano, 2005, vol. 2, 155–160.