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Effectiveness diffusion coefficient in nickel catalyst grain determined by measurements of catalytic reaction rate♣

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1. INTRODUCTION

Industrial catalysts are porous solids of a very complicated spatial structure, because they contain pores of various character, dimensions and shapes. Catalysts textural properties are usually described by several features such as: porosity, internal surface and pore dimension distribution but they are only indirectly connected with their activity. An effective diffusion coefficient catalyst grain is a very important catalyst property, because it defines completely mass transport within the grain and it is directly connected with the catalytic properties.

A complete characteristics method of diffusion properties of a nickel catalyst for methane steam conversion is proposed. The method is based on a determination of the effective diffusion coefficient by a measurement and comparison of a catalytic reaction rate in diffusion and kinetic regions. The estimation method of catalyst grain diffusion properties is illustrated by measurement results for two catalysts of very different grain properties.

Two nickel catalysts of very different grain properties were prepared. 20% NiO were introduced by impregnation to two carriers formed from aluminas: (1) α-Al_2O_3 and (2) γ-Al_2O_3, which had different grain size and forms (Raschig rings and balls) and also different textural properties: porosity, internal surface and pore size (Table 1).

♣This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65th birthday

2. MEASUREMENT OF REACTION KINETICS

Carbon oxide methanation was used as a test reaction for kinetic measurements. Measurements were carried out with gradientless methods in a kinetic region (on a catalyst of crushed grains in a Zieliński type reactor [1]) and in a diffusion region (on a catalyst of non- crushed grains in a tank reactor with a stirrer [2]). A mixture of hydrogen and small amount of CO was fed to the reactor from a steal cylinder. Gas streams were fed by ERG type controllers. The CO, CO_2 and CH_4 content was determined in concentration ranges measured in vppm with PU-4500 gas chromatograph fitted with a methanizer and a FID detector. Gas flow was measured with a bubble meter. Reaction rate was calculated from mass balance of the reactors.

Reaction rate was measured on catalysts which textural properties are presented in Table 1. Measurement conditions were as follows:

- type of test reaction: CO methanation;
- catalyst grain size [mm]: non-crushed grains (Table 1), or crushed grains 0.16-0.25;
- sample size: 4 rings, or 60 balls, or 60 mg of crushed catalyst;
- measurement temperature [^{o}C]: 300;
- measurement pressure: atmospheric;
- inlet CO/H_2 content [vppm]: 6000.

Measurements were carried out on a catalyst reduced wit hydrogen and stabilized for 4 hours at temperature of 500°C. Measurement and calculation results are presented in Table 2.

Tab. 1. Physicochemical properties of individual catalyst grain.

Lp.	Grain form	Grain size	Apparent density	Average pore size	Grain porosity	Internal surface BET
		[mm]	[g/cm^3]	[cm]	[%]	[m^2/g]
1	Rings $Ø_{out}·Ø_{in}·h$	16.66 · 8.9 · 16.38	2.41	1.66E-05	40.5	2.85
2	Balls	4.34	1.50	1.16E-06	70.4	80.7

3. MEASUREMENT AND CALCULATION RESULTS

Methanation rate at temperature of 300°C interpolated to a small CO content (200 vppm) was used for calculation of effective diffusion coefficient. At such small CO content we can assume the first order reaction. The ratio of reaction rates measured on crushed and on non- crushed grains indicates used of degree internal surface effectiveness factor „η". Thiele modulus Φ is an inverse function of „η" for low values of factor ($\eta < 0{,}2$). Thiele equation in the below form was used for calculation of effective coefficients of internal diffusion.

$$\Phi = L * \sqrt{k_k / D_{ef}}$$

where: $\Phi = 1/\eta$ – Thiele modulus [-], $L = V_z/S_z$ – the ratio of grain volume to surface [m], k_k – reaction rate constant in the kinetic region in the first-order reaction [1/s], D_{ef} – effective coefficient of internal diffusion [m^2/s].

Tab. 2. Results of kinetic measurements and calculations.

Lp.	Grain form	r_{CH4} at 200 vppm CO	Effectiveness factor „η"	Thiele modulus Φ	D_{ef}	Tortousity factor
		[Ndm^3_{CO}/g·h]	[%]	[-]	[m^2/s]	[-]
1	Rings	4.15E-03	2.6	38	2.22E-06	6.3
	Crushed grain	1.58E-01	100			
2	Balls	1.83E-02	4.8	21	1.36E-06	2.3
	Crushed grain	3.80E-01	100			

4. CONCLUSIONS

A characteristics method of diffusion properties of nickel catalysts for methane steam conversion has been proposed. The method comprises the measurement of catalytic reaction rates in kinetic and diffusion regions. Such estimation of diffusion properties of catalyst grains can be applied to evaluation of tortuosity factor for catalysts used in processes of simple kinetics, such as: methane conversion, carbon oxide methanation, benzene hydrogenation, and carbon oxide shift conversion.

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5. REFERENCES

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