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Acetylene hydrogenation over Pd/MgO nanocrystalline system: Effect of the synthesis route on catalytic performance

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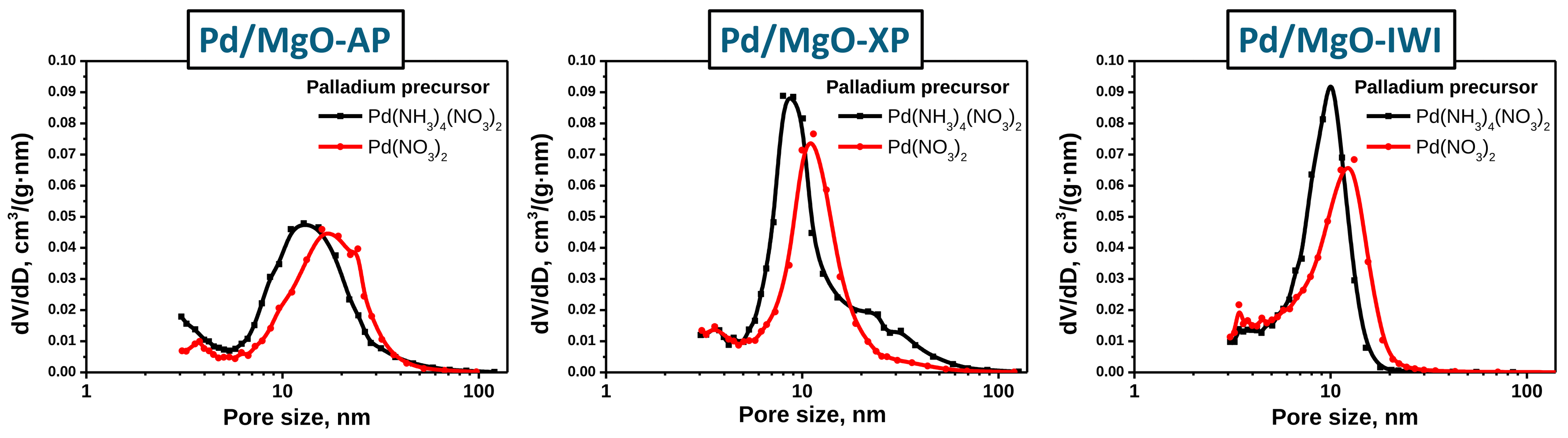
Introduction

Ethylene is the most versatile petrochemical feedstock for the production of polyethylene, ethanol, ethylene oxide, ethylene glycol, styrene, dichloroethane, and many other chemical products. The process of hydrogenation of acetylene into ethylene can be used both to purify ethylene from an impurity of alkyne, which is formed at the stage of pyrolysis of crude oil while getting C_2H_4 [1], and for direct ethylene production from acetylene [2]. Most often, palladium-based metal systems are used as catalysts for the acetylene hydrogenation reaction due to their high catalytic activity. The efficiency of such catalysts is determined primarily by the dispersity and the electronic state of palladium, which depend on the strength of its interaction with the support and the acid-basic properties of the latter. When Al_2O_3 is used as a support, the acid sites can promote the side reactions of oligomerization. Whereas in the case of magnesium oxide, the base sites, interacting with Pd, can add some electronic density to the metal particles on the surface [3, 4].

[1] A. Borodziński, G. Bond, Catal. Rev. Sci. Eng. 48 (2006) 91-144.
[2] D.A. Shlyapin, D.V. Glyzdova, T.N. Afonasenko et al. Kinet. Catal. 60 (2019) 446-452.
[3] Z. Guan, M. Xue, Z. Li, R. Zhang, B. Wang, Appl. Surf. Sci. 503 (2020) 144142.
[4] Y. He, J. Fan, J. Feng, C. Luo, P. Yang, D. Li, J. Catal. 331 (2015) 118-127.

Characterization of the materials

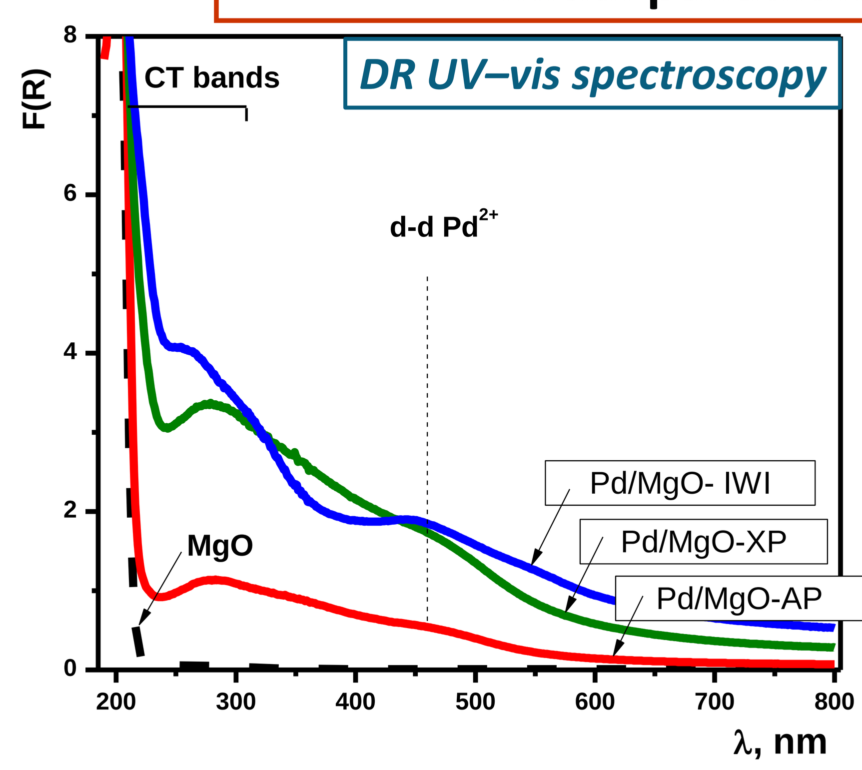


Sample	Preparation method	Palladium precursor	A_{BET}, m²/g	V_{pore}, cm³/g	D_{av}, nm	D_{mf}, nm
1A	Aerogel	$Pd(NH_3)_4(NO_3)_2$	228	0.86	15.0	12.8
1B		$Pd(NO_3)_2$	170	0.86	20.2	15.9
2A	Xerogel	$Pd(NH_3)_4(NO_3)_2$	225	0.95	16.8	7.8
2B		$Pd(NO_3)_2$	184	0.69	15.0	11.4
3A	Impregnation	$Pd(NH_3)_4(NO_3)_2$	160	0.50	12.5	10.1
3B		$Pd(NO_3)_2$	134	0.56	16.7	13.2

D_{av} – Average Pore Diameter (4V/A)
D_{mf} – BJH Desorption Most Frequent Pore Diameter

- **Using $Pd(NO_3)_2$ as Pd precursor results in the larger pore size.**
- **Both xerogel preparation and incipient wetness impregnation lead to narrower pore size distribution in comparison to aerogel preparation.**
- **The choice of the metal precursor and the support preparation route makes an impact on porous structure of catalyst.**

Initial palladium state (500 °C, air)

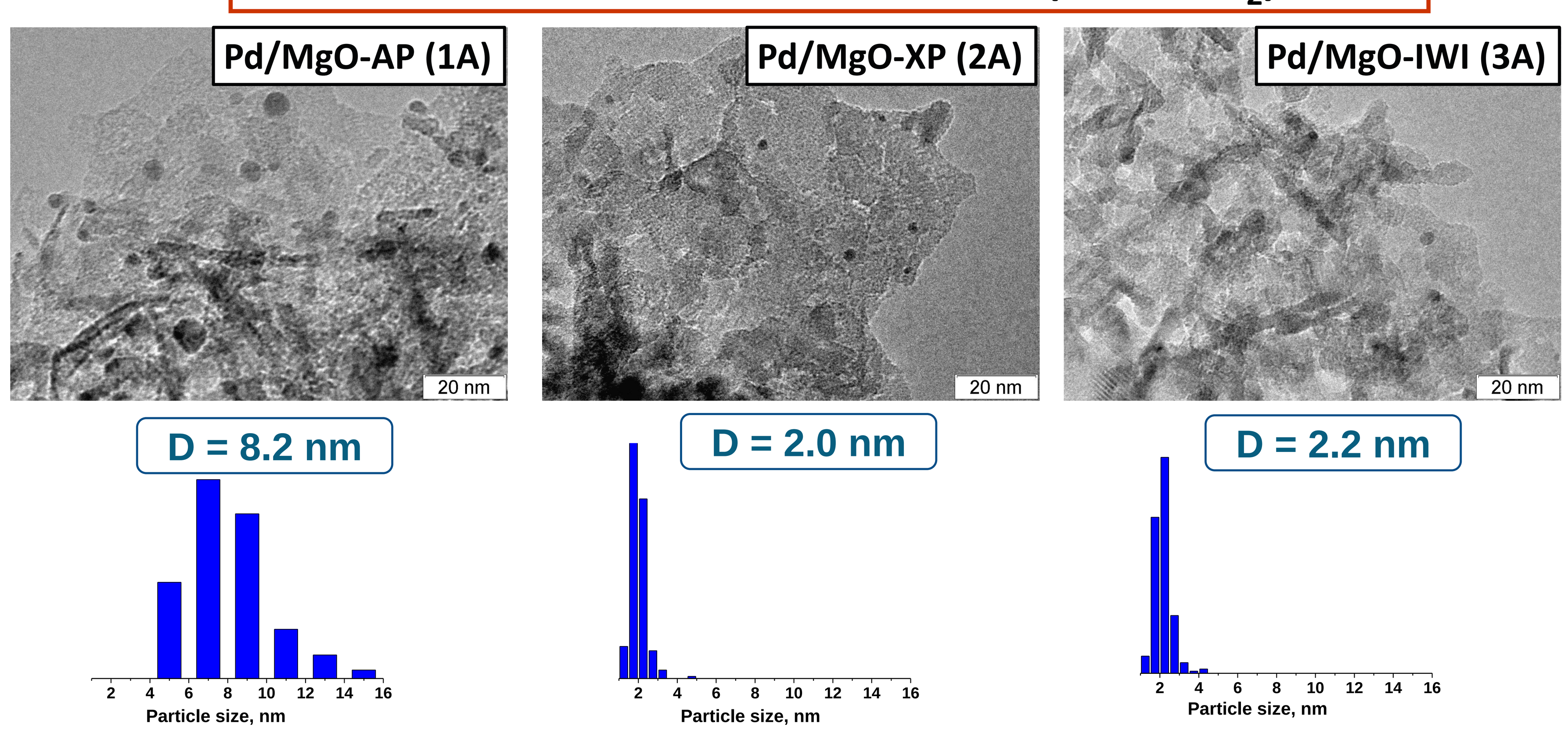


	Sample	Eg, eV	Sample	Eg, eV
Pd/MgO-AP	1A	2.31	1B	2.29
Pd/MgO-XP	2A	1.98	2B	2.25
Pd/MgO-IWI	3A	2.05	3B	2.13

E_g – band gap calculated via Tauc plot

- **In the case of Pd/MgO-AP samples the lowest E_g values and, therefore, the smallest PdO particles and the highest proportion of Pd^{2+} ions.**
- **Low intensity of Pd/MgO-AP spectrum testifies towards a part of the particles being located in the bulk of the support.**

Palladium state after reduction (500 °C, H_2)



Using transmission electron microscopy, it was shown that the palladium particles have a spherical shape and are uniformly distributed over the support. The average size of palladium particles depends on the synthesis method: the most dispersed particles (D = 2.0 – 2.2 nm) are formed in the case of xerogel and impregnation methods. The aerogel prepared samples contain palladium particles of ~ 8.2 nm in size.

Acknowledgement

This work was supported by the Ministry of Science and Higher Education of the Russian Federation [project No. AAAA-A21-121011390054-1]. Characterization of the samples was performed using the equipment of the Center of Collective Use "National Center of Catalysts Research".
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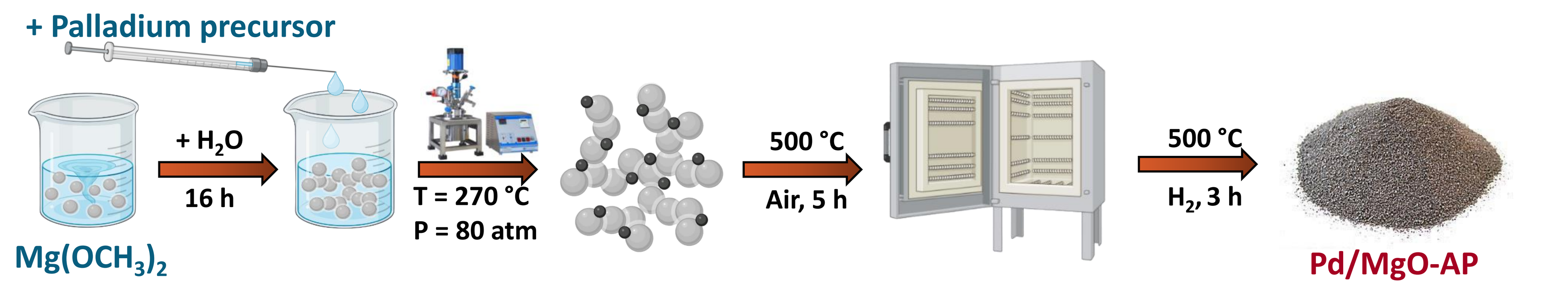
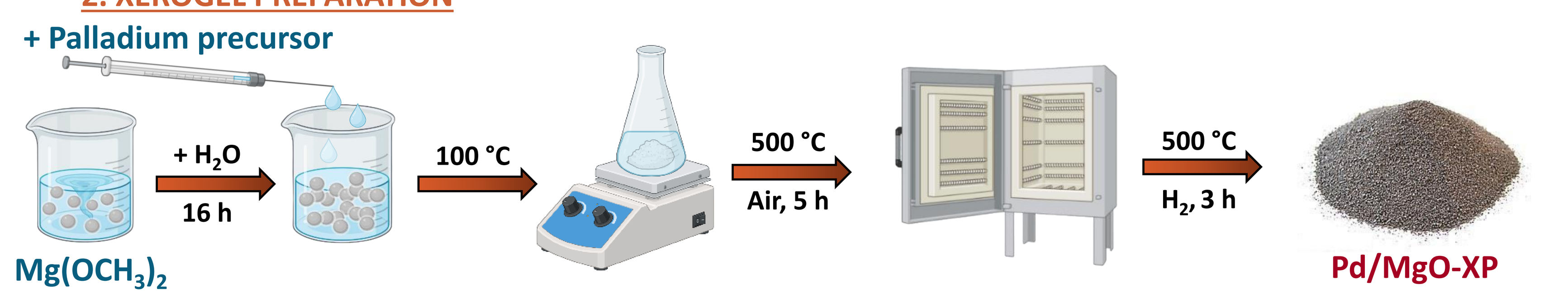
Synthesis

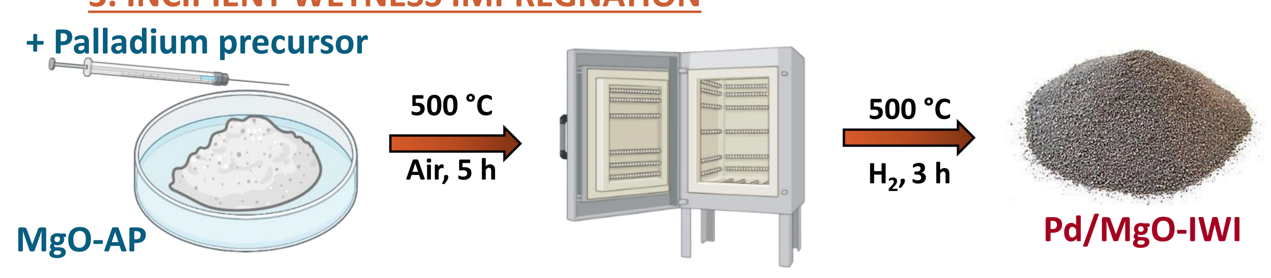
1. AEROGEL PREPARATION



2. XEROGEL PREPARATION

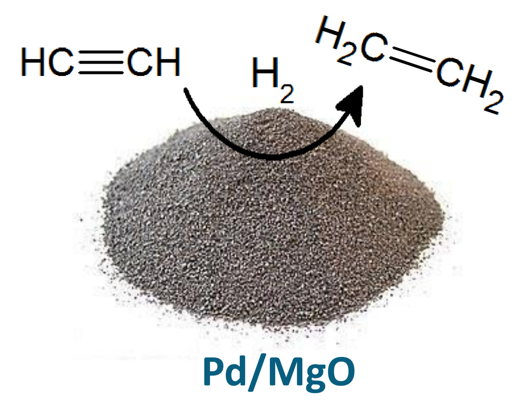


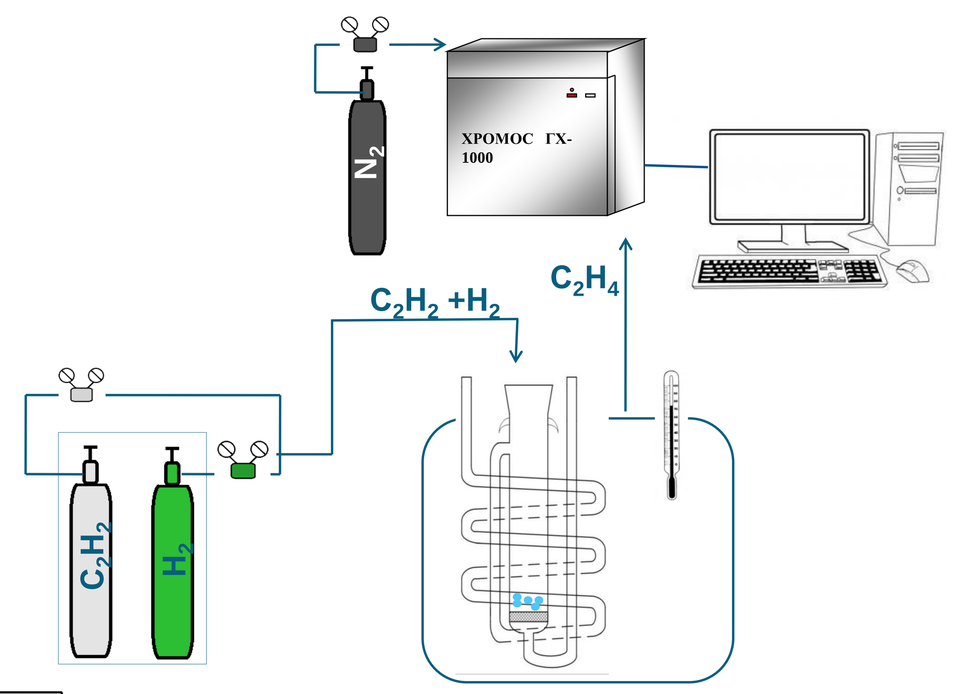
3. INCIPIENT WETNESS IMPREGNATION



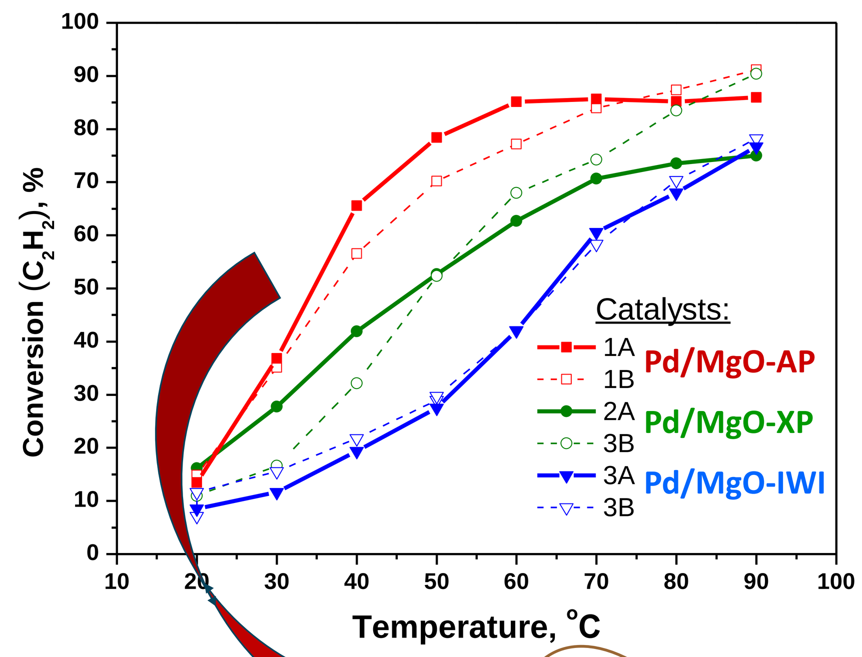
Three methods of synthesis were used to prepare 1% Pd/MgO.

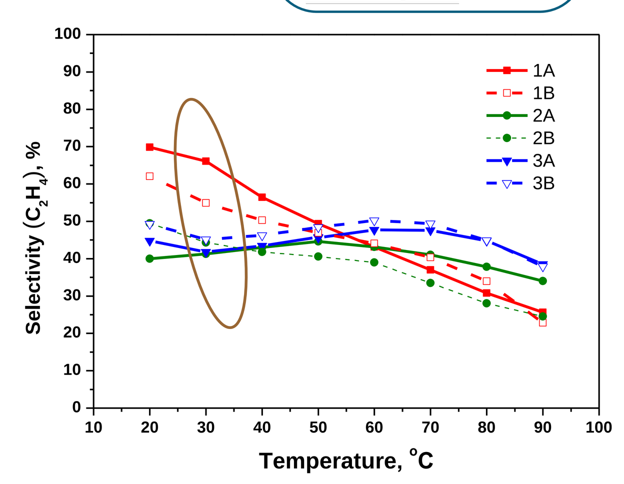
Catalytic activity

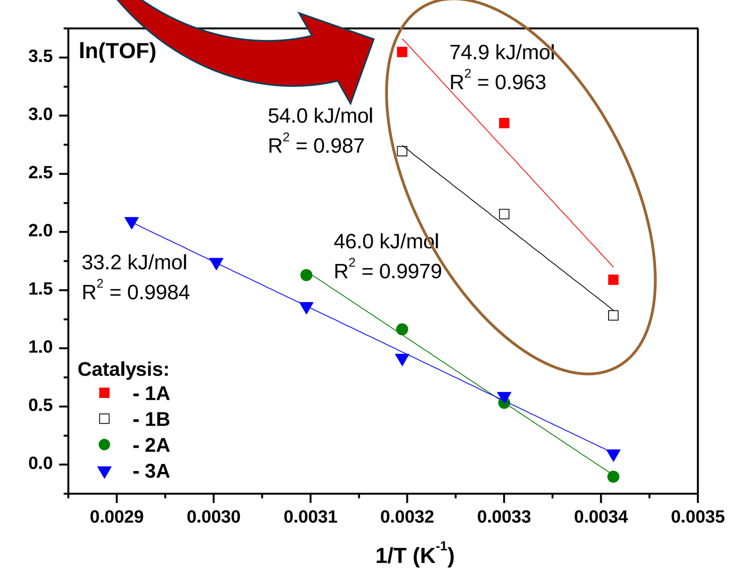


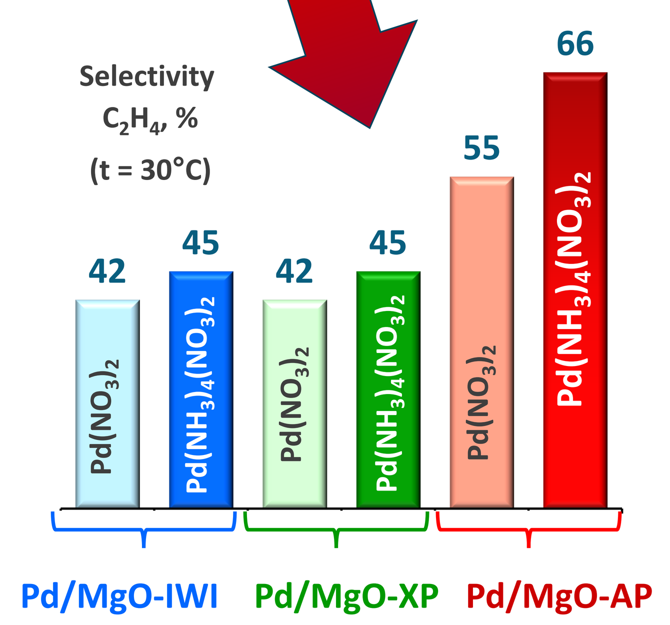


Catalytic tests in the acetylene hydrogenation reaction were performed in a flow regime, in a stream of a gas mixture containing 4 vol.% C_2H_2 in hydrogen within the temperature range from 20 to 90 °C.









- It can be concluded from Arrenius plot data and conversion curves, that the activity of the aerogel supported palladium catalysts increases faster then activity of the other samples.
- For the aerogel prepared catalysts, 50% of acetylene transformed at 35 °C, while for XP- and IWI-prepared samples such conversion values were achieved at noticeably higher temperatures of 50 and 65 °C, respectively. It was found that the maximum ethylene selectivity (60 – 70%) is also typical for the aerogel-prepared sample at 25 °C.
- The Pd/MgO catalyst synthesized by the airogel method from $[Pd(NH_3)_4](NO_3)_2$ exhibit the highest acetylene conversion and ethylene selectivity compared to samples obtained by two other methods.

Conclusions

- In this work, a series of 1 wt.% Pd/MgO catalysts was synthesized. Such methods as aerogel preparation, xerogel preparation, and incipient wetness impregnation were used. It was shown that the preparation route affects texture and dispersion of the active metal.
- The Pd/MgO catalysts were investigated in the process of acetylene hydrogenation to ethylene (4% C_2H_2 + 96% H_2; 20 – 90 °C). It was found that the aerogel method is promising for the synthesis of Pd/MgO catalyst for selective hydrogenation of acetylene to ethylene.