Highly dispersed Pd/MgO catalysts based on nanocrystalline MgO prepared via sol-gel method

Veselov G.B.[1], Ilyina E.V.[1], Shivtsov D.M. [1,2], Stoyanovskii V.O. [1], Vedyagin A.A[1]

1 – Boreskov Institute of Catalysis, Novosibirsk

2 – Novosibirsk State Technical University, Novosibirsk

E-mail: g.veselov@catalysis.ru

BOREKOV INSTITUTE OF CATALYSIS

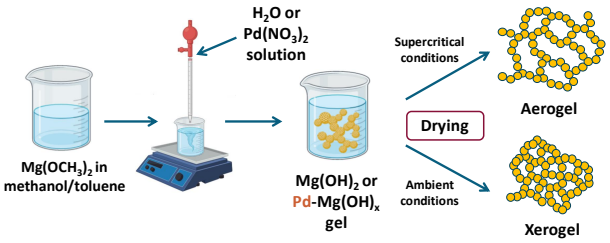
Introduction

Materials based on nanocrystalline magnesium oxide attract great attention of researchers. The main property of MgO is its pronounced basic properties. MgO nanoparticles find use in organic synthesis as heterogeneous basic catalysts of reactions such as aldol reaction, amide synthesis, Michael reaction and etc. [1]. MgO is a prospective sorbent material for the capture of CO_2 and chloroorganic compounds [2]. It is used as a support in traditional heterogenous catalysis in processes of dry reforming and CO_2 methanation.

However, MgO-based catalysts are not widely applied in industry. One of the reasons is the absence of large-scale manufacturing of such materials with high specific surface area (SSA). On the lab-scale level, one of the most prospective approaches is alkoxide sol-gel synthesis of $Mg(OH)_2$ gels followed by supercritical drying. This method is easily scalable and produces MgO with SSA as high as 350 m^2/g after calcination at 500 °C. Recently, we developed a modified **"one-step"** approach to the synthesis of two- and three- component oxide systems based on MgO [3-5]. In this approach, soluble inorganic salts serve as precursors. The parameters of the process such as pH can be adjusted to obtain optimal porous structure and dispersion of an active component.

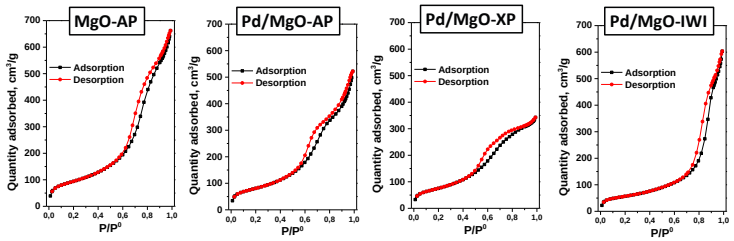
In this work the approach was applied to the preparation of 1 wt.% Pd/MgO catalysts. The samples were studied via nitrogen adsorption, TEM and UV-vis spectroscopy. Catalytic activity in CO oxidation was evaluated in prompt thermal aging (PTA) mode to test thermal stability.

The modified sol-gel approach



Sample	Preparation method
MgO-AP	Conventional sol-gel approach with supercritical drying
Pd/MgO-AP	One-step sol-gel approach with supercritical drying
Pd/MgO-XP	One-step sol-gel approach with drying under ambient conditions
Pd/MgO-IWI	Incipient wetness impregnation of MgO-AP
Pd/MgO-EDTA	EDTA-assisted impregnation of MgO-AP

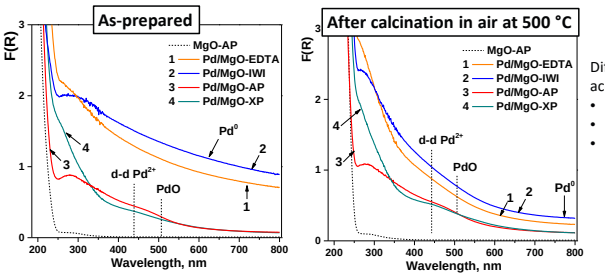
Characterization of the materials



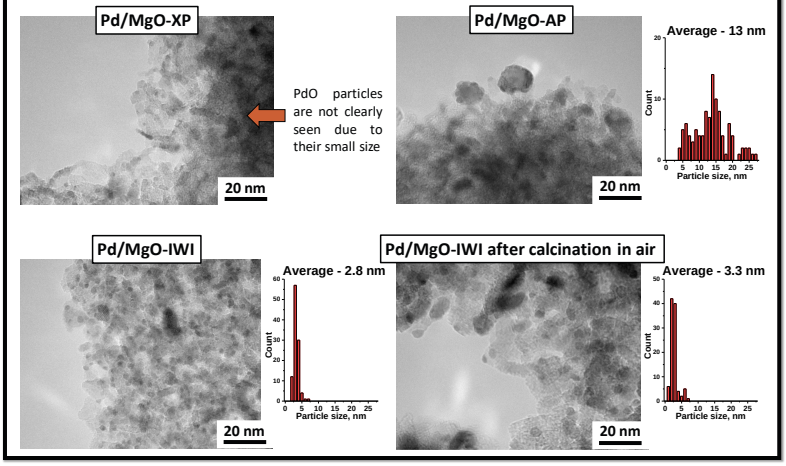
Sample	A_{BET}, m^2/g	V_p, cm^3/g	$4V_p/A_{BET}$, nm	Modes of PSD, nm	
				Adsorption	Desorption
MgO-AP	328	1,002	12,2	8	6.5
Pd/MgO-XP	280	0,53	7,6	5.2	4.5
Pd/MgO-AP	296	0,808	10,9	6.1	5.5
Pd/MgO-IWI	205	0,934	18,2	4, 14.5	11
Pd/MgO-EDTA	296	0,951	12,8	7.9	7

- The samples are mesoporous with large surface area; supercritical drying allowed avoiding shrinkage of the porous structure.
- Introduction of Pd during the sol-gel synthesis leads to the formation of a denser structure with smaller pores.
- Impregnation results in enlargement of MgO crystallites.

Characterization of the palladium state

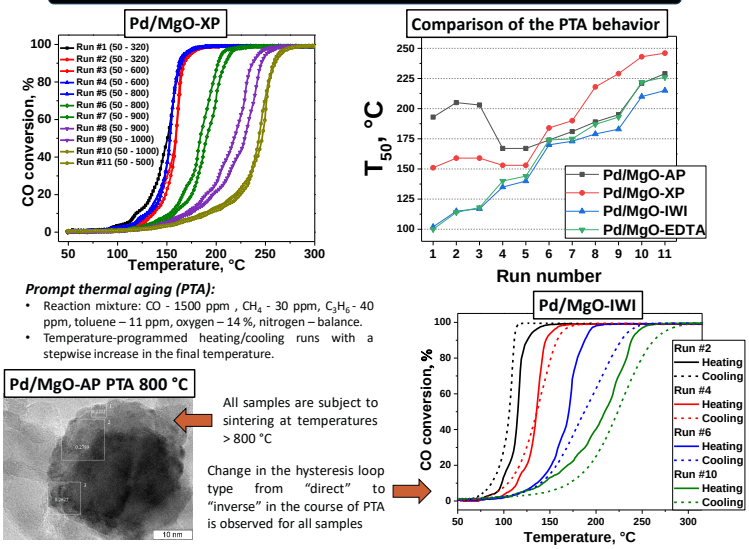


Different state of Pd according to UV-vis DRS:
- XP – Pd^{2+}, small PdO
- AP – larger PdO
- IWI and EDTA – Pd^0 and not completely oxidized after treatment at 500 °C.



PdO particles are not clearly seen due to their small size

Catalytic activity and thermal stability

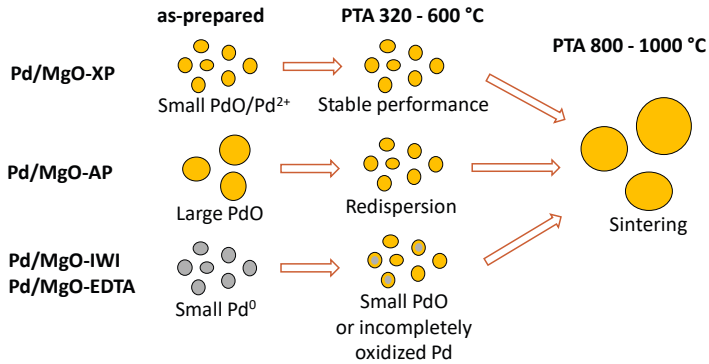


Prompt thermal aging (PTA):
- Reaction mixture: CO - 1500 ppm , CH_4 - 30 ppm, C_3H_6 - 40 ppm, toluene – 11 ppm, oxygen – 14 %, nitrogen – balance.
- Temperature-programmed heating/cooling runs with a stepwise increase in the final temperature.

All samples are subject to sintering at temperatures > 800 °C

Change in the hysteresis loop type from "direct" to "inverse" in the course of PTA is observed for all samples

Proposed scheme of the evolution of the palladium state during PTA



Conclusions

A series of Pd/MgO catalyst based on nanocrystalline MgO with the developed texture was prepared. Exceptionally high specific surface area and pore volume were obtained for the aerogel-derived samples. Pd/MgO-XP prepared via the "one-step" sol-gel method demonstrated high dispersion of the active component. In contrast, Pd/MgO-AP sample prepared via the supercritical drying approach showed large PdO particles. Impregnation of aerogel-prepared support has led to the formation of dispersed Pd^0 particles. As a result, the samples demonstrated different behavior during prompt thermal aging in oxidative medium. Small metal particles are oxidized at 320-600 °C and undergo sintering at 800-1000 °C. Redispersion takes place in the case of large PdO (> 10 nm) particles, whereas smaller PdO particles were stable until 800 °C. In all cases, the change of the type of the CO conversion temperature hysteresis loop from "direct" to "inverse" is observed.

Literature

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