



PHYSICAL CHEMISTRY 2021

15th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume II

The Conference is dedicated to the

*30th Anniversary of the founding of the Society of Physical
Chemists of Serbia*

and

100th Anniversary of Bray-Liebhafsky reaction

**September 20-24, 2021
Belgrade, Serbia**

Title: Physical Chemistry 2021 (Proceedings) **ISBN** 978-86-82475-40-8

Volume II: ISBN 978-86-82475-39-2

Editors: Željko Čupić and Slobodan Anić

Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia

Publisher: Society of Physical Chemists of Serbia

For Publisher: S. Anić, President of Society of Physical Chemists of Serbia

Printed by: "Jovan", <Printing and Publishing Company, 200 Copies

Number of pages: 6+388, Format A4, printing finished in December 2021

Text and Layout: "Jovan"

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PHYSICAL CHEMISTRY 2021

*15th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

Organized by

*The Society of Physical Chemists of
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in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

*Borekov Institute of Catalysis Siberian Branch of
Russian Academy of Sciences*

and

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INFLUENCE OF COBALT LOADING ON THE PHYSICAL-CHEMICAL PROPERTIES OF PILLARED CLAY - SUPPORTED COBALT

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ABSTRACT

The aluminum pillared clay (AP) was synthesized and impregnated with various cobalt loadings (x%CoAP, x=1, 3, 5, and 10 wt.%) by incipient wetness impregnation method. All samples were characterized by using X-ray powder diffraction (XRPD), inductively coupled plasma optical emission spectroscopy (ICP-OES) and low temperature N₂ physisorption techniques. The chemical analysis confirmed the successful incorporation of cobalt in all impregnated samples. Nevertheless, only cobalt oxide (Co₃O₄) was identified for samples having higher cobalt contents. Furthermore, different cobalt loading was mainly affected the microporous region in such way that micropore surface area decreased with the increase of cobalt.

INTRODUCTION

Pillared clays (PILC) as materials with permanent micro and/or mesoporosity and high surface area have been attracting considerably attention as catalytic support materials. Such interest rose from the fact that PILC can be easily prepared from the cheap, non-toxic and naturally available clays [1,2]. Recently, aluminum pillared clay-supported cobalt (CoAP) was found to be a promising catalyst for both catalytic oxidation of dye [2] and electrochemical determination of glucose [1]. In order to exploit the full potential of this catalyst, further optimization was requested. This paper discusses the influence of cobalt loading on physical-chemical properties of CoAP as the first step in designing a catalyst with optimal performance.

EXPERIMENTAL

Preparation of AP and x%CoAP samples

Montmorillonite clay from the Source Clays Repository–The Clay Minerals Society, Wyoming, was used for pillaring. Pillaring solution with OH⁻/Al³⁺ molar ratio of 2.0 was used for the synthesis of pillared clay. The detailed preparation of pillared clay was previously described [2]. The obtained pillared clay was denoted as AP. Cobalt was introduced into AP by impregnation using the incipient wetness impregnation method [3] in order to obtain Co-based catalysts (CoAP). The impregnation was performed by gradual addition of 0.89 cm³ of 0.3, 1, 1.7, and 3.3 mol dm⁻³ of Co²⁺ solution in order to introduce 1 wt.%, 3 wt.%, 5 wt.%, and 10 wt.% of cobalt, respectively into AP powder. Then the samples were dried at 85 °C for 2 h and subsequently at 110 °C, overnight. The obtained samples were then calcined at 450 °C for 6 h and denoted as x%CoAP where x=1, 3, 5, 10 represents the weight percentage of cobalt.

Characterization of AP, and x%CoAP samples

The content of cobalt in x%CoAP samples was determined by ICP-OES technique using a iCAP 6500 Duo ICP Spectrometer (Thermo Fisher Scientific, Cambridge, UK). The samples were prepared by microwave digestion (Advanced Microwave Digestion System, ETHOS 1, Milestone) and analysed with iTEVA operating software. X-ray powder diffraction data of AP, and x%CoAP samples were obtained using a Philips PW 1710 X-ray powder diffractometer (CuK α radiation, $\lambda = 0.1542$ nm).

Textural properties of samples were determined from the nitrogen adsorption/desorption isotherms at $-196\text{ }^{\circ}\text{C}$ using a Sorptomatic 1990 Thermo Finnigan.

RESULTS AND DISCUSSION

The ICP-OES results (Table 1) confirmed the incorporation of cobalt in the impregnated samples in amounts about 80% of theoretical. According to X-ray structural analysis (Fig. 1.) the presence of montmorillonite (Mt) and quartz (Q) was identified in all samples [4]. For samples impregnated with lower cobalt contents (up to 4.13 wt.%), no peaks related to cobalt oxide were detected. In contrast, the characteristic reflections of the cubic Co_3O_4 phase at 31.3° , 36.9° and 59.4° [4] were clearly visible in the diffractograms of the samples with higher cobalt content. Moreover, with the increase of cobalt content from 4.13 wt.% to 7.85 wt.% the intensity of all diffraction peaks corresponding to Co_3O_4 increased.

Isotherms of all samples (Fig. 2.) belong to the II type with the H3 type of hysteresis loop for $p/p_0 > 0.4$ characteristic for montmorillonite containing clays with aggregated planar particles and slit-shaped types of pores [2].

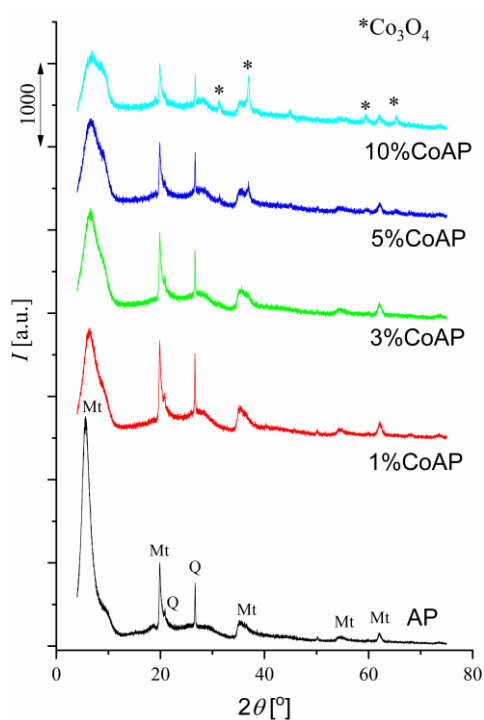


Figure 1. XRPD patterns of AP and x%CoAP samples

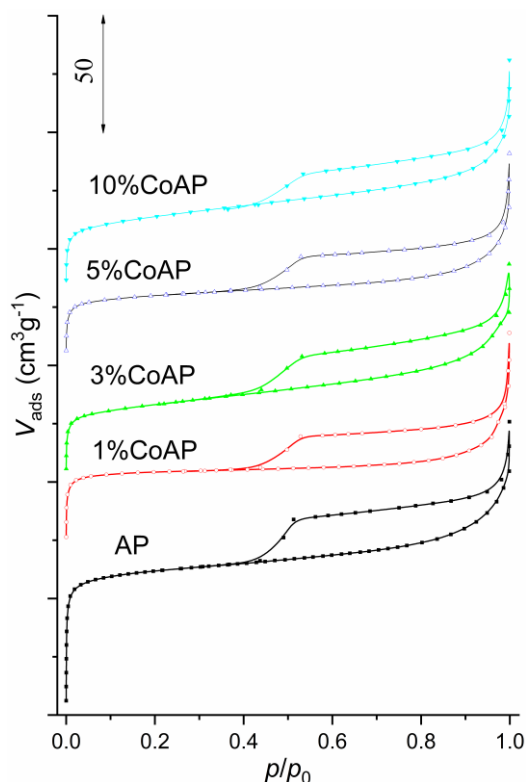


Figure 2. N_2 adsorption-desorption isotherms of AP and x%CoAP samples

The highly developed mesoporous and microporous structure of pillared sample was affected by impregnation process. The impregnation with cobalt resulted in decrease of specific surface area in both mesoporous and microporous range of pores (Table 1). The process parameter that had the highest impact on textural properties was regime of heat treatment after impregnation since all cobalt impregnated samples had comparable values for the specific surface area. Differences in the surface area between samples impregnated with different amounts of cobalt are almost negligible in mesoporous region (with exception of S_{BET} for 1%CoAP and S_t for 10%CoAP). On the other hand,

in microporous region there is more noticeable trend. The specific surface area (S_{mic}) decreased with the increase of cobalt loading.

Sample	Co content (wt.%)		S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{mic} ($\text{m}^2 \text{g}^{-1}$)	S_{t} ($\text{m}^2 \text{g}^{-1}$)
	theoretical	experimental			
AP	-	-	211	199	12
1%CoAP	1	0.79	146	133	13
3%CoAP	3	2.55	124	107	17
5%CoAP	5	4.13	123	109	14
10%CoAP	10	7.85	129	76	53

S_{BET} – specific surface area (Brunauer, Emmett, Teller - 3 parameter equation); S_{t} – mesopore surface area t-Plot (Lippens and de Boer, using universal Harkins, Jura standard isotherm), S_{mic} – micropore specific surface ($S_{\text{BET}} - S_{\text{t}}$)

CONCLUSION

This study continues our research devoted to development of the pillared clay - supported cobalt based catalysts (CoAP). It has been found that Co loading affected the phase composition and textural properties. The increase of cobalt loading above 4 wt.% favored the formation of Co_3O_4 . The lower cobalt loading were not detected by XRPD as separate crystalline phases. Heat treatment after impregnation is probably responsible for the same derogation effect on textural properties (in both micro and mesopore region) of x%CoAP in comparison to AP. The cobalt content had impact only in microporous range. The specific surface area (S_{mic}) decreased with the increase of the cobalt loading. Correlation between findings of this work and the catalytic performance of x%CoAP in two catalytic processes i.e. electrochemical oxidation of glucose and catalytic oxidation of dye is still ongoing.

Acknowledgement

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-9/2021-14/200026).

REFERENCES

- [1] Mudrinić T, Marinović S, Milutinović-Nikolić A, Jović-Jovičić N, Ajduković M, Mojović Z, et al. Novel non-enzymatic glucose sensing material based on pillared clay modified with cobalt. *Sensors Actuators B Chem* 2019;299:126976. <https://doi.org/https://doi.org/10.1016/j.snb.2019.126976>.
- [2] Marković M, Marinović S, Mudrinić T, Ajduković M, Jović-Jovičić N, Mojović Z, et al. Co(II) impregnated Al(III)-pillared montmorillonite–Synthesis, characterization and catalytic properties in Oxone® activation for dye degradation. *Appl Clay Sci* 2019;182:105276. <https://doi.org/https://doi.org/10.1016/j.clay.2019.105276>.
- [3] Pinna F. Supported metal catalysts preparation. *Catal Today* 1998;41:129–37. [https://doi.org/https://doi.org/10.1016/S0920-5861\(98\)00043-1](https://doi.org/https://doi.org/10.1016/S0920-5861(98)00043-1).
- [4] JCPDS, 1990. International Center for Diffraction Data. Joint Committee on Powder Diffraction Standards (JCPDS) , Swarthmore, USA, pp. 1990.