Structural Analysis of Ru/Ce₁₋ₓZrₓO₂ catalysts for the Carbon Dioxide Methanation

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Introduction

Scientific studies aimed at reducing the impact of human activities on the environment are of great interest. Reduction of the amount of carbon dioxide emissions into the atmosphere is one of the challenges. The catalytic process of carbon dioxide methanation is of practical importance due to its use for CO_2 utilization with simultaneous synthesis of energy carrier, methane.

Ruthenium-based catalysts are known to be highly active in methanation processes at relatively low temperatures (200-250°C) and low loading of an active component (~1-5 wt.% %) [1-3]. It has been reported that the most effective catalysts are based on easily reduced oxide supports, for example, cerium dioxide Ru/CeO_2 and mixed cerium-zirconium oxides $Ru/Ce_{1-x}Zr_xO_2$. Despite a large number of studies dealing with the activity of such catalysts, there is little information about their structural organization and structure of ruthenium-containing particles. Structural study on such systems requires the use of methods that allow one to solve structure at the atomic level and to identify ultra dispersed species. One of the effective method is the X-ray atomic pair distribution function analysis (PDF analysis). It also allows us to probe the short-range atomic order.

In this work, the results of structural studies of the supported $Ru/Ce_{1-x}Zr_xO_2$ heterogeneous catalysts are highlighted. A wide range of structural methods is used: powder X-ray diffraction (XRD) methods and PDF analysis. Some attention will be paid to the study on structural evolution of catalyst upon its activation via reduction with use of in situ XRD.
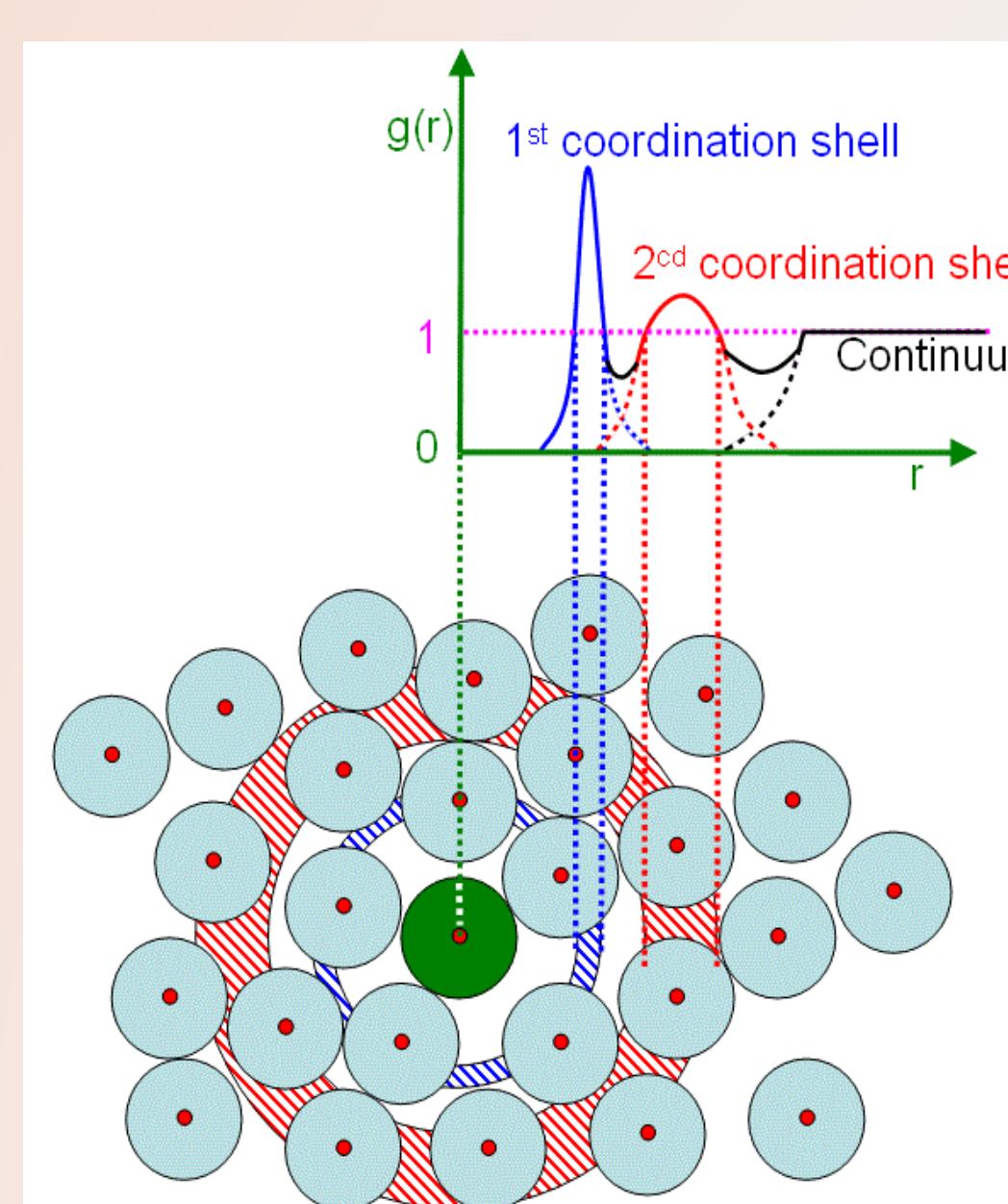
Structural analysis of Ru/CZ_ox and Ru/CZ_H₂

Ex situ XRD of Ru/CZ_ox and Ru/CZ_H₂

1. The well-crystallized phase of ruthenium oxide RuO_2 is detected in the XRD pattern of the Ru/CZ_ox sample
2. According to XRD analysis, Ru/CZ_H₂ catalyst doesn't contain any crystallized ruthenium-containing phases. The crystal lattice parameter of $Ce_{1-x}Zr_xO_2$ is decreased, there is its structure distortion

Pair distribution function (PDF) analysis of Ru/CZ_H₂

The differentiul d-PDF was obtained by subtracting from the catalyst PDF of the support PDF. The observed atomic correlations don't correspond to RuO_2 or Ru^0 structure. The detected arrangement of atoms corresponds to the oxide with a fluorite-type structure, characterized by smaller lattice parameter a ≈ 5.33 Å.
Detecting atomic configurations with the fluorite-type structure is explained by the incorporation of ruthenium cations into the surface layers of the support structure.

Samples and methods

Samples:

Supported heterogeneous catalysts $Ru/Ce_{1-x}Zr_xO_2$ were synthesized by sorption-hydrolytic deposition method (Ru/CZ_ox is calcined in air, Ru/CZ_H₂ is reduced in a hydrogen-containing atmosphere)

Methods:

i. *Ex situ & in situ XRD*
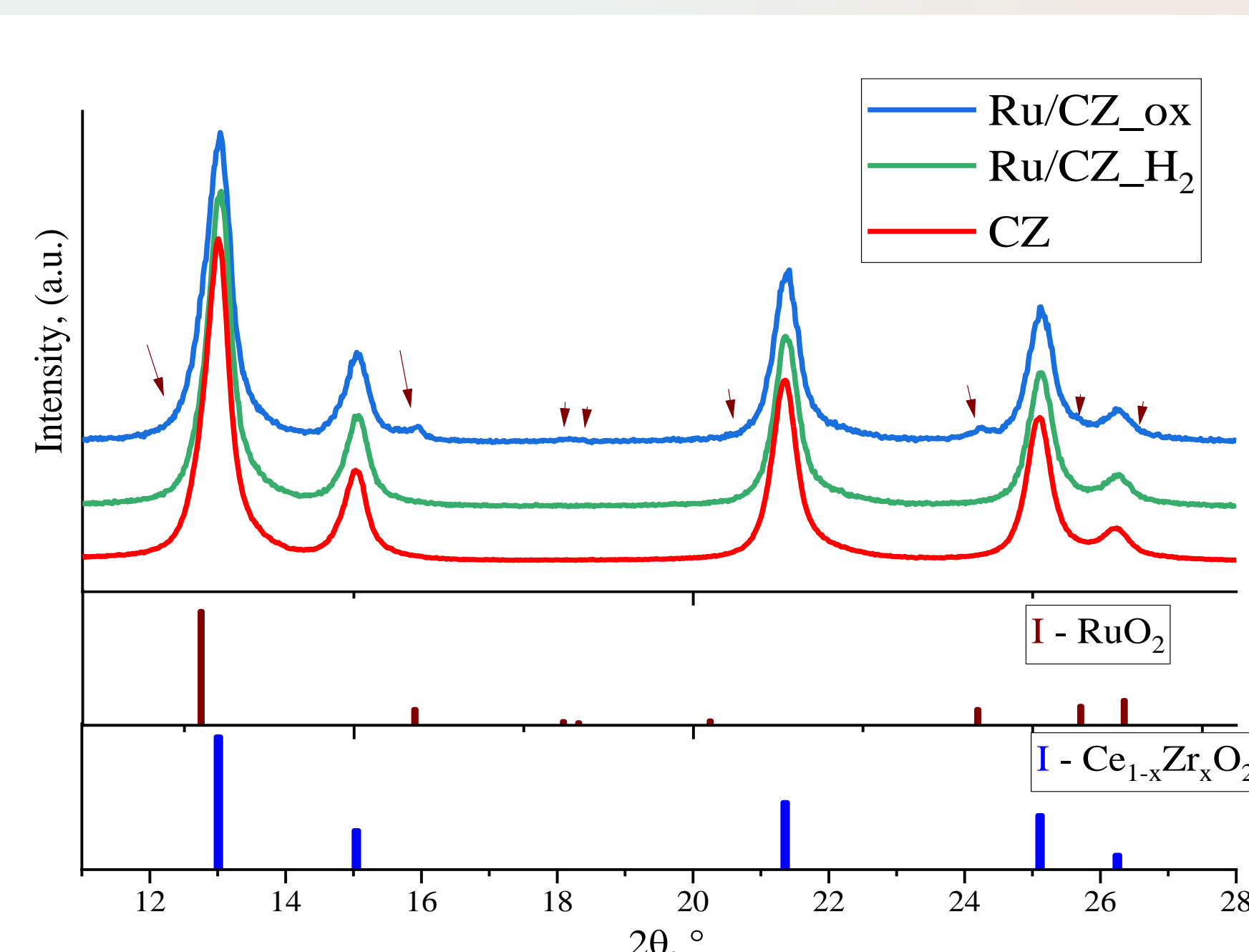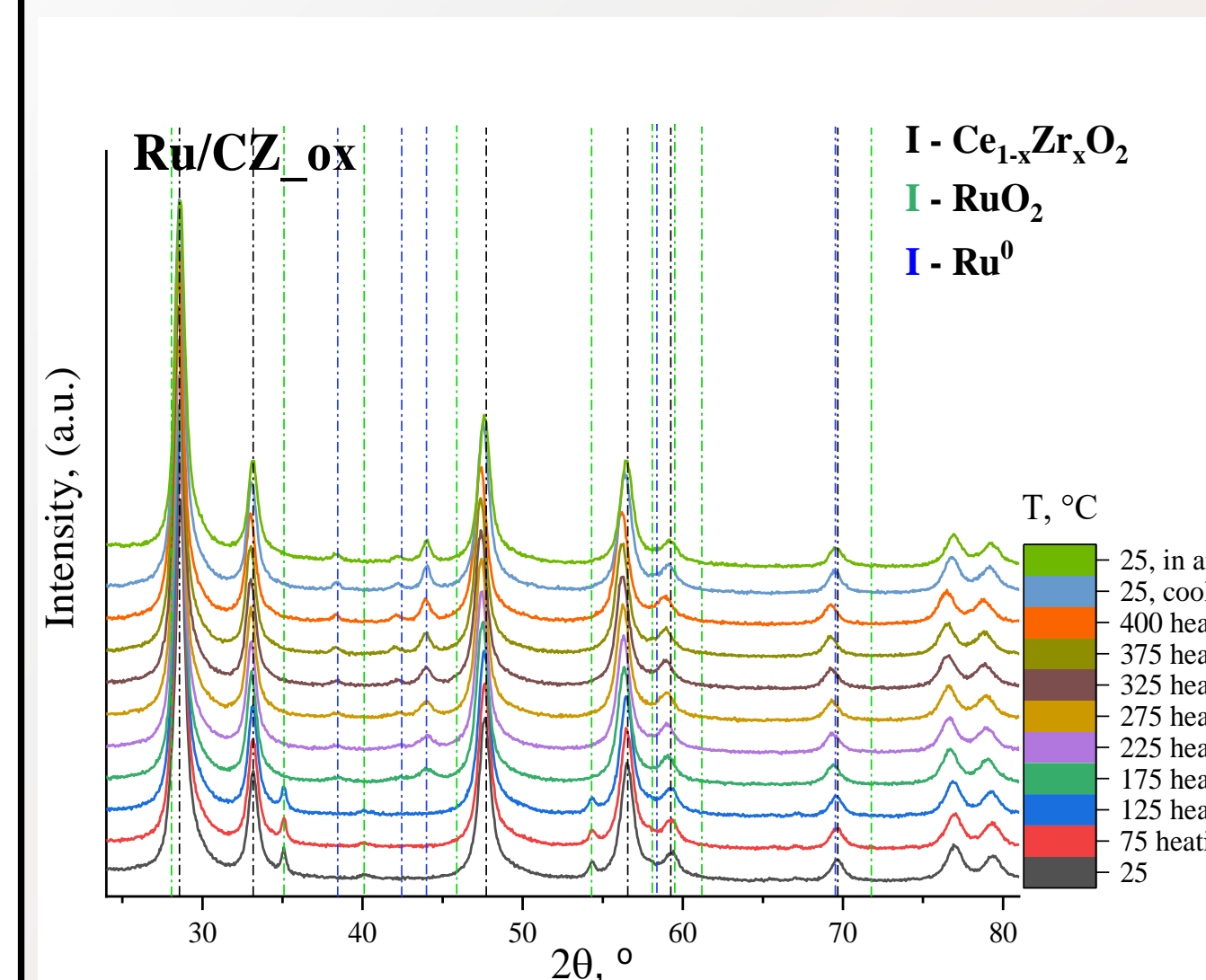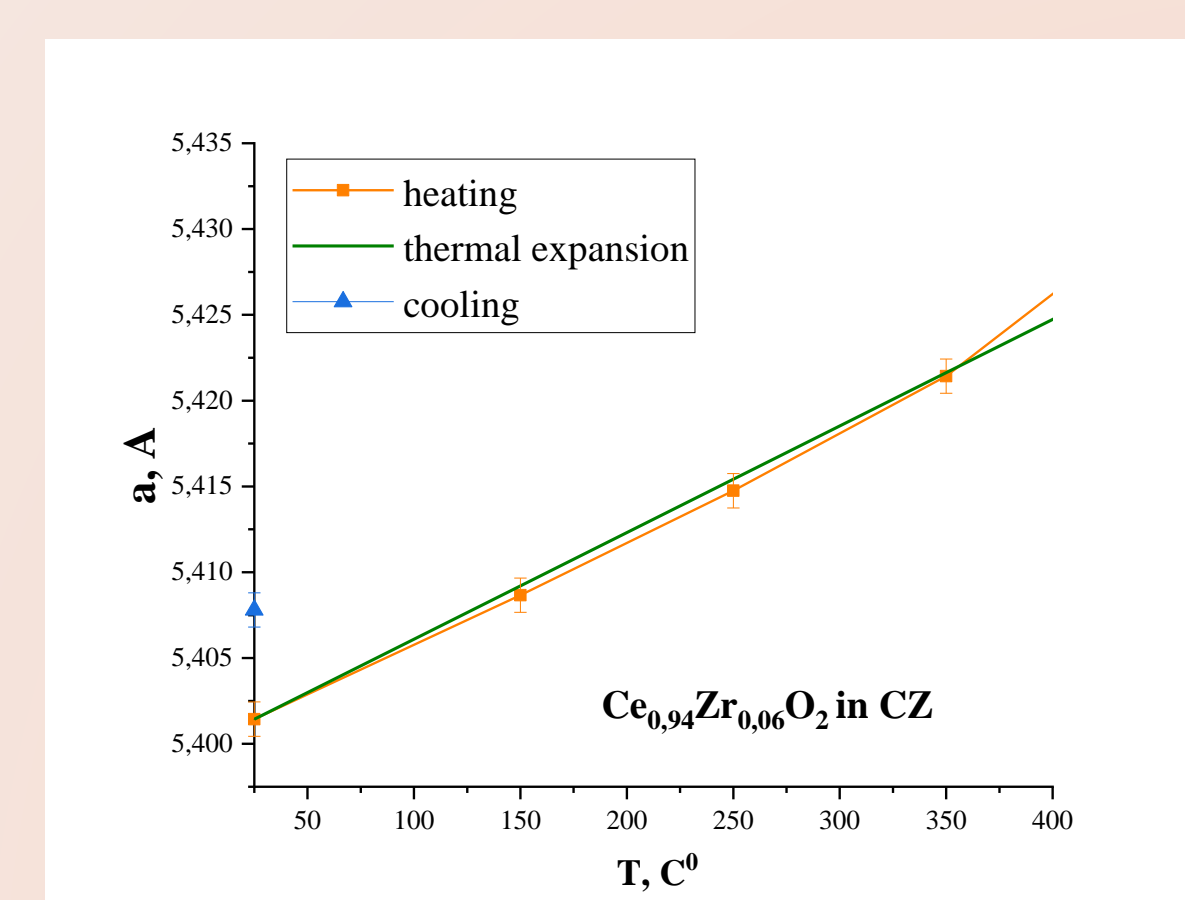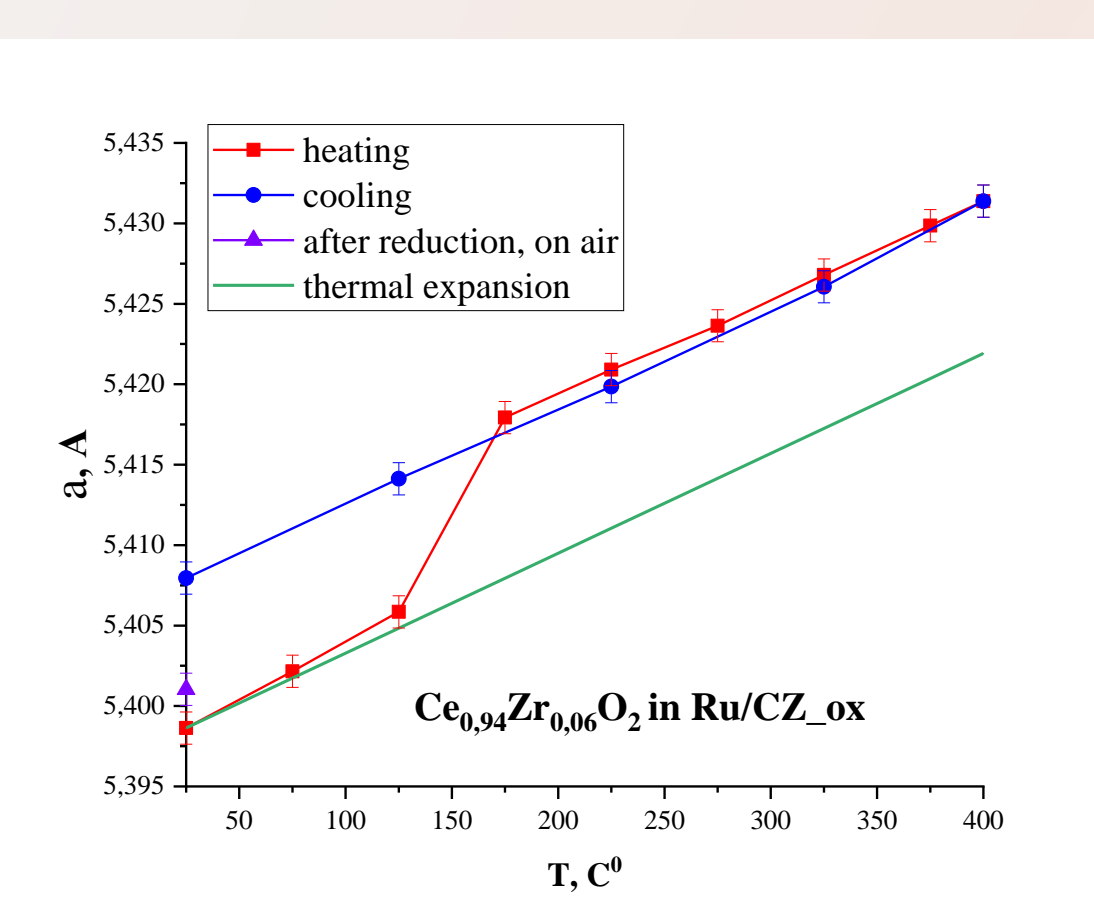ii. *Pair distribution function (PDF) analysis*

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty F(Q)\sin(Qr)dQ$$

- the probability function to find a pair of atoms at a distance **r** from each other

- Position of coordination maxima
- Peak Intensity

- Interatomic distances
- Atomic coordinates
- Average size of atomic ordering (crystallite size)

In situ XRD study of reductive activation of Ru/CZ_ox catalyst

The reduction of ruthenium oxide to the metallic ruthenium Ru^0 state is detected at 175°C.
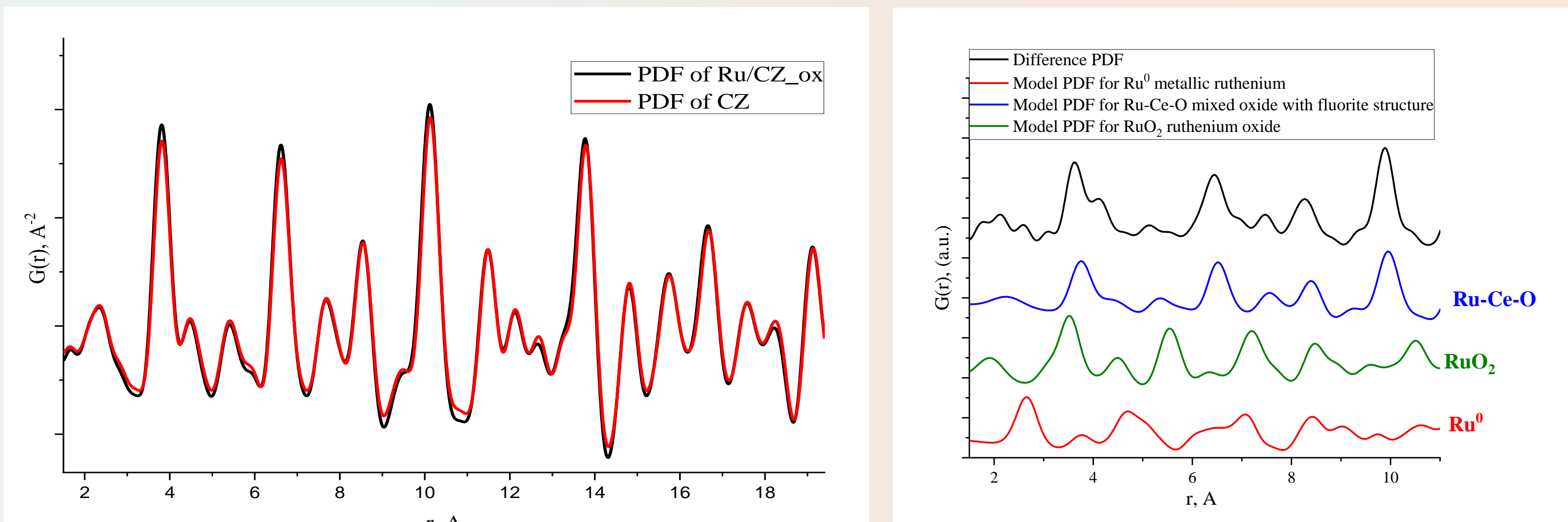

Starting from 175°C, change of the $Ce_{1-x}Zr_xO_2$ lattice parameter does not correspond to the expected linear growth caused by lattice thermal expansion. The formed metallic Ru^0 particles promote a partial reduction of the support surface due to the hydrogen spillover effect.

Conclusion

I. The study of supported $Ru/Ce_{1-x}Zr_xO_2$ catalysts revealed dependence of dispersion and structure of active particles on heat treatment conditions of catalyst precursors in various gases. The calcination of the catalyst precursor in air leads to the formation of well-crystallized ruthenium oxide RuO_2. Heat treatment of the catalyst precursor in a hydrogen-containing gas mixture promotes the formation of highly dispersed ruthenium compounds and enhances the interaction of the Ru species with the support surface.

II. During the activation process of the $Ru/Ce_{1-x}Zr_xO_2$ catalyst in a reductive hydrogen flow, the particles of ruthenium oxide RuO_2 are reduced to the metallic state Ru^0. Formed metallic Ru^0 particles promote the partial reduction of the $Ce_{1-x}Zr_xO_2$ oxide surface due to the hydrogen spillover effect.

References

[1]. Kim A. et al. Mesoporous TiO2 support materials for Ru-based CO2 methanation catalysts //ACS Applied Nano Materials. – 2019. – T. 2. – №. 5. – C. 3220–3230.
[2]. López-Rodríguez S. et al. Effect of Ru loading on Ru/CeO2 catalysts for CO2 methanation //Molecular Catalysis. – 2021. – T. 515. – C. 111911.
[3]. Rynkowski J. M. et al. Characterization of Ru/CeO2-Al2O3 catalysts and their performance in CO2 methanation //Reaction Kinetics and Catalysis Letters. – 2000. – T. 71. – C. 55-64.

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