

Investigation of CO-induced segregation on the surface of bimetallic Pd-Ag catalyst by CO-DRIFTS and XPS

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Introduction

The phase composition and the element ratio at the surface and in the bulk are often differing from each other in case of bimetallic Pd-based catalytic systems, which is caused by surface segregation. The driving force of this process is the tendency to decrease the surface energy in bimetallic system. Surface rearrangement can be controlled by the adsorption of different adsorbate molecules (CO, O₂, C₂H₂, etc), leading to enrichment of the catalyst surface with a component whose binding energy with the adsorbate molecule is higher. Since the structure of surface layers of bimetallic catalytic system depends on sample treatment conditions (temperature, exposure time), the surface segregation can be used as a simple and convenient method of controlling the surface structure of catalyst.

Catalyst preparation

2%Pd-4%Ag/Al₂O₃ («Sasol»),
S_{БЭТ} = 56 м²/г

Wetness impregnation by palladium and silver nitrates

Air drying at 25°C

Calcination in air at 550°C 4 h

Reduction in 5%H₂/Ar flow at 580°C, 3 h

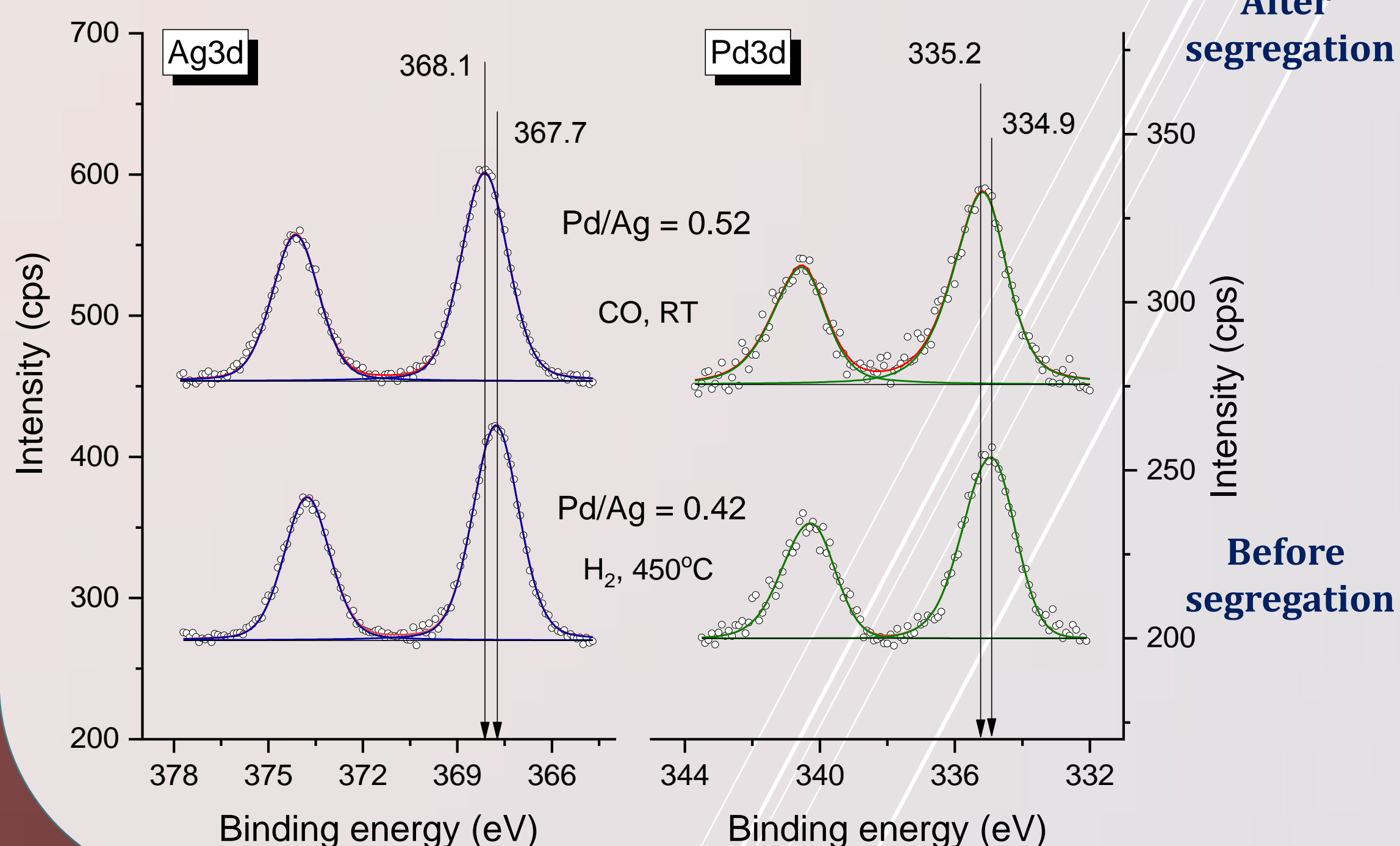
Calcination in air at 450°C 4 h

Reduction in 5%H₂/Ar at 500°C, 3 h

Repeat 5 cycles

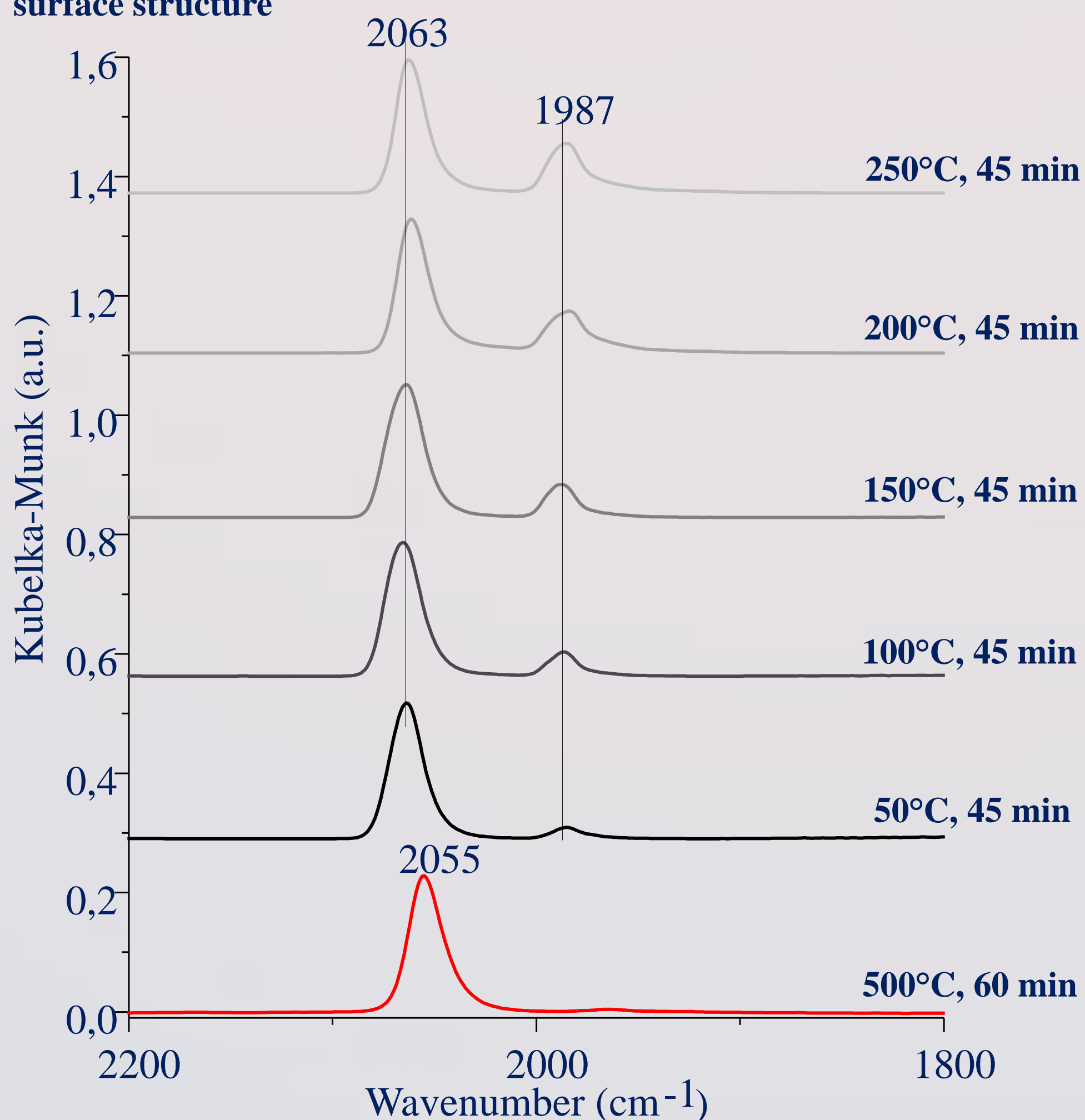
XPS investigations

For performing the XPS experiments the SPECS NAP-XPS system with the backfilling configuration was used. According obtained results, after CO exposure (2 mbar, 1 h) the Pd/Ag atomic surface ratio increased from 0.42 to ~0.52 indicating segregation of palladium atoms to catalyst surface.

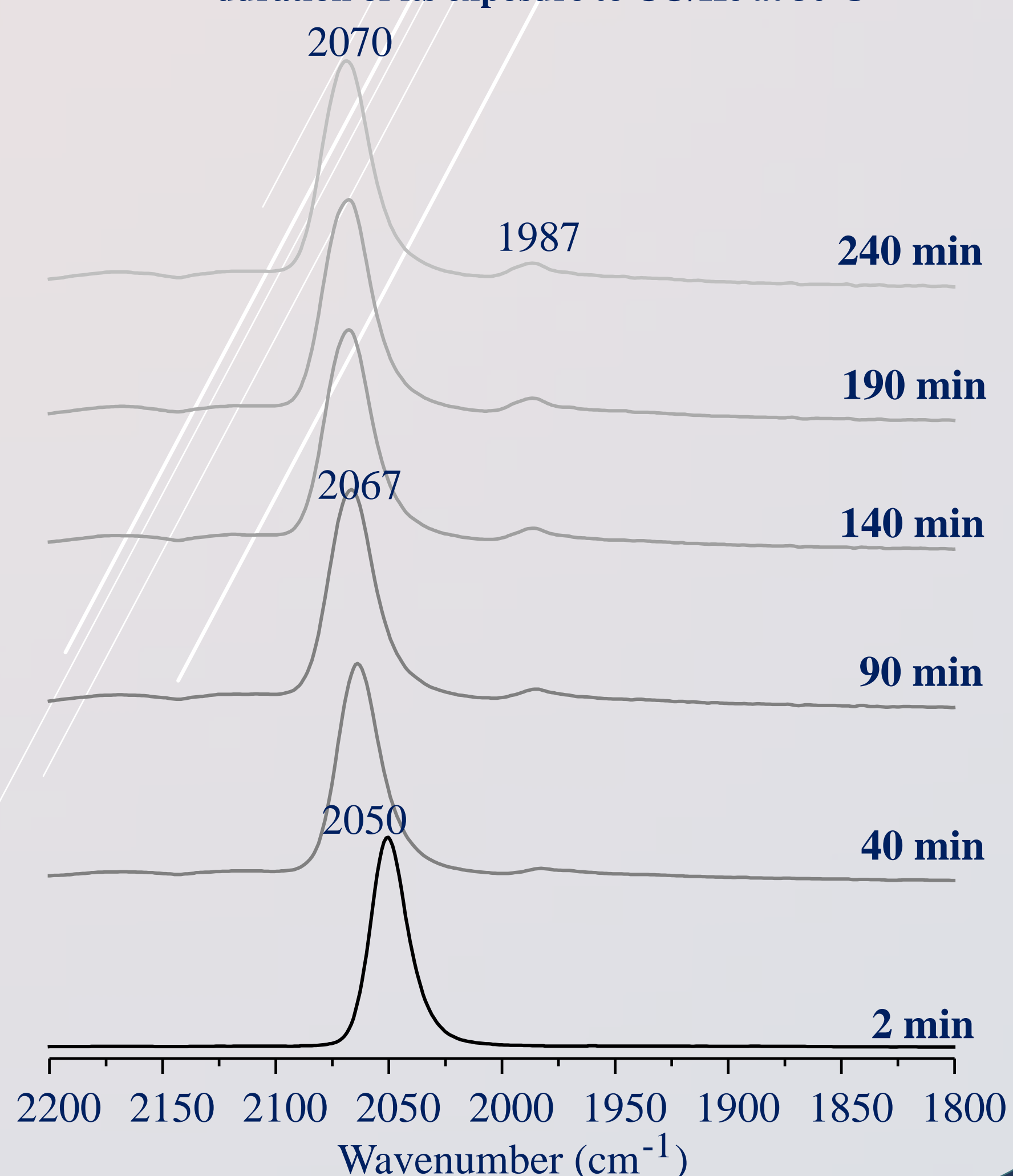


DRIFT spectroscopy of chemisorbed CO

Dependence of the treatment temperature in CO atmosphere on the catalyst surface structure



Dependence of DRIFT spectra of the PdAg₂/Al₂O₃ catalyst on the duration of its exposure to CO/He at 50°C



Acknowledgments

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Literature

1. A.Yu. Stakheev, N.S. Smirnova, P. V. Markov, G. N. Baeva, G. O. Bragina, A. V. Rassolov, I. S. Mashkovsky, Kinet. Catal. 59 (2018) 610.
2. Mamatkulov M., Yudanov I.V., Bukhtiyarov A.V., Prosvirin I.P., Bukhtiyarov V.I., Neyman K.M. // J. Phys. Chem. C., 2019, 123, 8037–8046

Conclusions

- CO-induced segregation of Pd leads to enrichment of palladium on the catalyst surface, which observed by XPS and DRIFTS; the temperature and time of CO exposure are the key factors affecting this process;
- The shift of peak from 2050 to 2070 cm⁻¹ in DRIFT spectra can be a result of the appearance of palladium atoms in the second coordination sphere or in the subsurface layer;
- During catalyst treatments the intensity of absorption bands corresponding to bridge-bonded CO increases significantly, which is associated with transformation of some part of monoatomic Pd₁ centers into «dimeric» Pd₂ sites.