

## Supporting Information

# The Origin of the Size Effect in the Oxidation of CO on Supported Palladium Nanoparticles

Vasily V. Kaichev <sup>1,\*</sup>, Andrey A. Saraev <sup>1</sup>, Aleksandr V. Fedorov <sup>2</sup> and Evgeny Yu. Gerasimov <sup>1</sup>

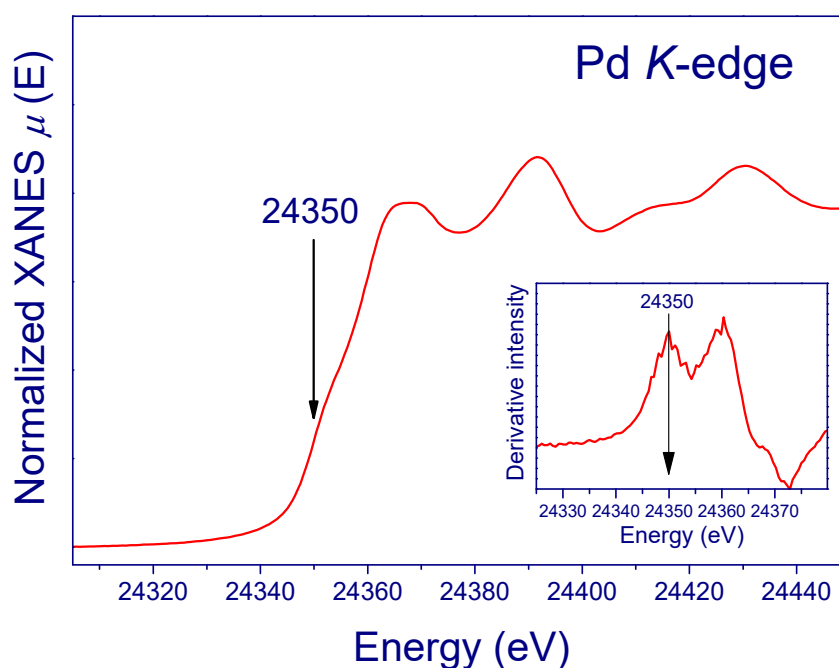
<sup>1</sup> Department of Catalyst Research, Boreskov Institute of Catalysis, Novosibirsk 630090, Russia; asaraev@catalysis.ru (A.A.S.); gerasimov@catalysis.ru (E.Y.G.)

<sup>2</sup> Department of Catalyst Discovery and Reaction Engineering, Leibniz-Institut für Katalyse e.V., 18059 Rostock, Germany; aleksandr.fedorov@catalysis.de

\* Correspondence: vvk@catalysis.ru

### X-ray absorption spectroscopy study

The XAS experiments were carried out at Beamline P64 at the high brilliance storage ring PETRA III at DESY (Hamburg, Germany). The storage ring was operated at 6 GeV with a constant ring current of 100 mA. The experimental station was described in detail elsewhere [1]. In short, the synchrotron radiation was provided by a 90 pole undulator. The radiation was monochromatized using a double-crystal monochromator with Si(311) crystals. To reduce higher harmonics, two silicon X-ray mirrors were used. The monochromator was calibrated by setting the first inflection point on the rising edge of the Pd K-edge spectrum of palladium foil at 24350.0 eV [2,3]. Note that the first inflection point occurs on the rising edge of an unresolved shoulder that extends to  $\mu x \sim 0.5$  at  $E - E_0 \sim 5$  eV. The structure within the edge is more obvious in the first derivative of the XANES spectrum. The Pd K-edge XANES spectrum of Pd foil and the first derivative plot of the spectrum are presented in Figure S1.



**Figure S1.** The Pd K-edge XANES spectrum of Pd foil. The first derivative plot of the spectrum is presented in the inset.

### Catalytic activity tests

The catalytic tests were carried out using a gradientless reactor with a flow-circulating configuration at atmospheric pressure. The reactor consisted of a stainless-steel tube with a 25 mm inner diameter and a 75 mm length. The reactor was placed inside an electrical oven. The temperature was controlled with a K-type thermocouple attached to the external wall of the reactor. A fraction of the catalyst powder contained grains in the range of 0.2–0.6 mm. The catalyst loading was 1 g. The reactor was equipped with an external circulation pump that provided the constant space velocity of premixed reactants through the catalyst bed with more than 15 recirculations per minute; this provided the total mixing mode and the absence of temperature and concentration gradients. The reaction feed consisted of 1 vol.% CO, 10 vol.% O<sub>2</sub>, and the balance Ar. The gas flows were regulated separately with mass-flow controllers SEC-Z500 (Horiba Ltd., Japan). The space velocity of the feed was varied in the experiments from 100 to 1000 ml/min. A TEST-1 gas analyzer (BONER, Russia) equipped with an optical absorption infrared sensor was used for analysis of the gas phase at the reactor outlet.

The CO conversion ( $X$ ) was calculated by the following equation:

$$X = 1 - \frac{\dot{n}_{CO}^{out}}{\dot{n}_{CO}^{in}}$$

where  $\dot{n}_{CO}^{in}$  and  $\dot{n}_{CO}^{out}$  are the inlet and outlet molar flows of CO (μmol/s), respectively.

The rate of CO oxidation  $r_{CO}$  (μmol s<sup>−1</sup> g<sup>−1</sup>) was estimated by the following equation:

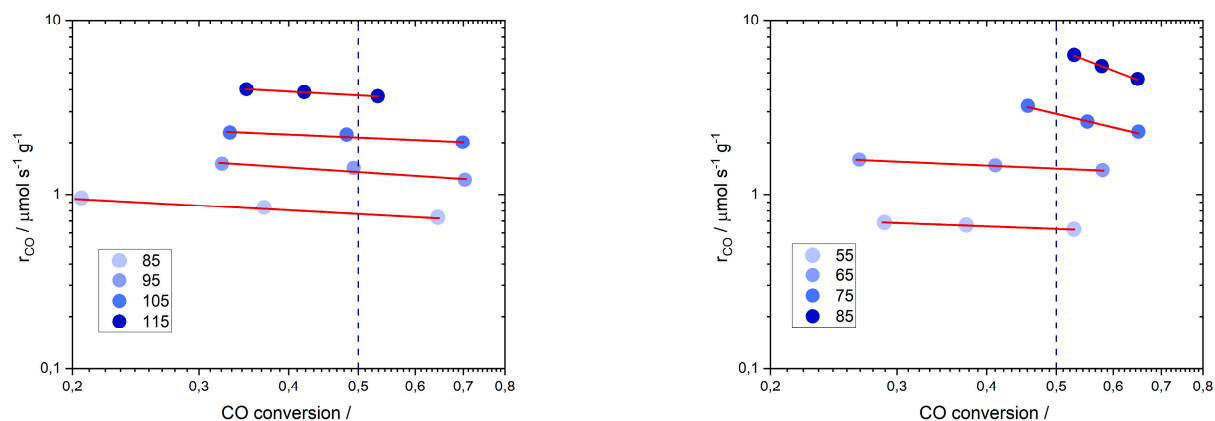
$$r_{CO} = \frac{\dot{n}_{CO}^{in} \cdot X}{m}$$

where  $m$  is the mass of the catalyst sample (g). At each reaction temperature, the rates of CO oxidation were determined at different inlet flows to obtain the rates  $r_{CO}$  at different conversions of CO. The obtained data representing the correlation between  $r_{CO}$  and  $X$  were approximated by the following formula:

$$\log r_{CO} = a \cdot \log X + b$$

where  $a$  and  $b$  are empirical parameters estimated to calculate the rate of CO oxidation at 50% CO conversion that was marked as  $r_{CO}^*$  (Figure S2). The rates  $r_{CO}^*$  obtained for different temperatures were used for estimating an apparent activation energy according to the Arrhenius equation:

$$r_{CO}^* = A \exp\left(-\frac{E_a}{RT}\right)$$



**Figure S2.** Correlations between the rate of CO oxidation and CO conversion for the Pd-3 (left) and Pd-1 (right) catalysts at different reaction temperatures.

A detailed description of the procedures for calculating the reaction rate and activation energy of the oxidation of CO is presented elsewhere [4].

## References

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4. Fedorov, A.; Saraev, A.; Kremneva, A.; Selivanova, A.; Vorokhta, M.; Šmíd, B.; Bulavchenko, O.; Yakovlev, V.; Kaichev, V. Kinetic and mechanistic study of CO oxidation over nanocomposite Cu–Fe–Al oxide catalysts. *ChemCatChem* **2020**, *12*, 4911–4921.