



Local reaction kinetics by imaging[☆]

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ABSTRACT

In the present contribution we present an overview of our recent studies using the “kinetics by imaging” approach for CO oxidation on heterogeneous model systems. The method is based on the correlation of the PEEM image intensity with catalytic activity: scaled down to the μm -sized surface regions, such correlation allows simultaneous local kinetic measurements on differently oriented individual domains of a polycrystalline metal-foil, including the construction of local kinetic phase diagrams. This allows spatially- and component-resolved kinetic studies and, e.g., a direct comparison of inherent catalytic properties of Pt(hkl)- and Pd(hkl)-domains or supported μm -sized Pd-powder agglomerates, studies of the local catalytic ignition and the role of defects and grain boundaries in the local reaction kinetics.

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1. Introduction

Already 40 years ago in an early work of Menzel and Kraemer it was demonstrated, that one can visually distinguish between the adsorbed CO and oxygen on the transition metal surface imaged by electron emission microscopy: different emission intensities were observed for the CO_{ad} and O_{ad} layers on Ru during the FEM (field electron microscopy) imaging [1]. Physical reason for this lies in the differing work function values of the CO- and oxygen-covered Ru surface (FEM is mainly a “work function” microscope [2]). Twenty years after these observations, a straight-forward correlation between the work function of the CO/O-covered surface and its catalytic activity in CO oxidation on Pt was experimentally established [3]. Thus it could be expected, that generally the image intensity in the “work function based” electron emission microscopes such as e.g. PEEM (photoemission electron microscopy), can provide information about the catalytic activity of the imaged surface, at least in CO oxidation. This relation was tacitly assumed in numerous PEEM observations of the CO oxidation on Pt-metal surfaces and also used for qualitative considerations [3–6]. The above studies were performed mainly for the single crystal surfaces (where the local activity corresponds to the averaged one), therefore the mass spectrometric (MS) measurements running parallel to PEEM observations, provided sufficient information about the reaction kinetics [4,5]. In the case of

the spatially-heterogeneous model systems, the MS approach meets, due to the data-averaging principle, its limits: MS does not distinguish between product species originating from different regions of the sample. Simplified model systems with active regions separated by sub-mm distances may allow for the use of a “scanning-MS” with gas sampling via a capillary leak [7]. Nevertheless, as for every scanning procedure, parallel measurements for many different locations are not possible with this method. Additionally, the products from neighboring locations might also attain the sampling nozzle-sniffer.

In turn, the correlation of the catalytic activity with the local work function opens the way to a “kinetics by imaging” approach where the information can be obtained solely from the work function dependent image intensity. Since such correlation must be valid also for the microscopically small areas of the surface, such local information can be obtained down to the resolution limit of the corresponding microscope. For PEEM this may allow spatially-resolved studies of local kinetic instabilities such as e.g. kinetic phase transitions on the μm - to tens of nm scale for the newest devices.

In the present contribution we present an overview of our recent studies using the “kinetics by imaging” approach for CO oxidation on heterogeneous model systems such as individual domains of polycrystalline Pt and Pd foils or Pd powder agglomerates supported by Pt foils.

2 Basics and experimental

As already mentioned above, the idea of the approach is based on the fact that the photoemission yield is directly dependent, via work

[☆] Dedicated to the 80th birthday of Professor Dietrich Menzel.

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function, on the adsorbate coverage. For the CO oxidation, it means that a CO or oxygen adlayer can be unambiguously identified from the PEEM image and, after the corresponding calibration, even the CO or oxygen surface density can be directly extracted from the PEEM image intensity [8]. Since the CO or oxygen coverage governs the rate of CO₂ formation the PEEM image intensity may serve as an indicator for the reaction rate. The CO oxidation on Pt-metals was intensively studied by PEEM since 1990s [3–6], including the observation of global kinetic transitions occurring on the single-crystal surfaces, such as Pt(111) [9], but the next logical step exploiting the parallel imaging principle of PEEM and the validity of the “catalytic activity – image intensity” correlation also for small areas, was not performed till 2010 [10]. The first studies of local kinetics using PEEM imaging were performed for polycrystalline Pt and Pd foils consisting on μm-sized grains forming a surface which exhibits differently oriented domains of corresponding size [10–13]. Fig. 1 shows an example of such a polycrystalline foil including the electron backscatter diffraction (EBSD) analysis of crystallographic orientation of particular domains. During the catalytic experiments, all the domains of the sample are exposed to the exactly identical conditions and information is collected, due to the parallel imaging principle of PEEM, simultaneously for all domains, providing thus perfect options for a comparison of the behavior of different orientations.

The experiments were performed in a UHV system consisting of two independently operated chambers connected with each other by a sample transfer line, thus allowing a common reactive gas atmosphere in the 10⁻⁴–10⁻⁹ mbar range. The “microscopy” chamber is equipped with a PEEM, (Staib instruments), a quadrupole mass spectrometer (QMS, MKS instruments), a LEED system (Omicron), a high purity gas supply system (O₂: 99.99%, CO: 99.97%) and sample preparation facilities for cleaning the sample by argon ion sputtering and annealing. The “spectroscopy” chamber is equipped with an XPS-system (Phoibos 100 hemispherical energy analyzer and XR 50 twin anode X-ray source, SPECS). The details of the experimental setup are described elsewhere [10–13].

The scheme of measurements is shown in Fig. 2: the global CO₂ formation rate in the CO oxidation reaction, originating from the whole sample is monitored by QMS yielding the *global* reaction kinetics. Simultaneously, PEEM is applied to visualize the reaction *in situ*. The contrast of a PEEM image which is formed by photoelectrons emitted from the surface upon UV light illumination is attributed to the local work function variations across the sample. These variations are sufficient to monitor the CO oxidation reaction. The digital analysis of the recorded video sequences allows to follow the reaction on the individual grains of the polycrystalline sample and to obtain *local* kinetic

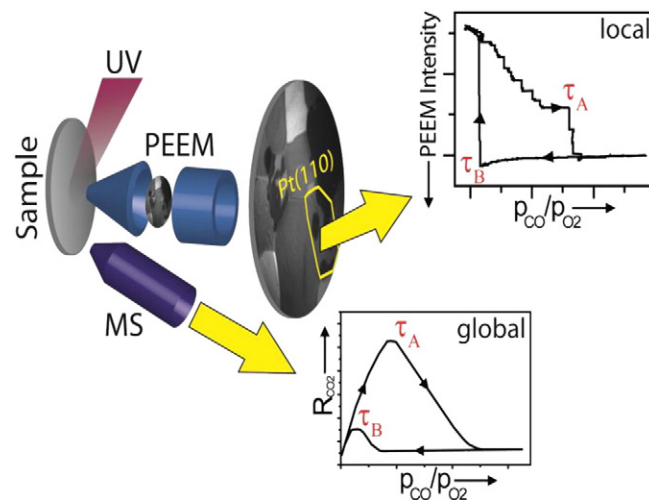


Fig. 2. Principle of the experiment. The ongoing catalytic reaction is simultaneously monitored by PEEM and MS. Global (averaged) MS data (lower inset) can be correlated with the spatially resolved data resulting from the intensity analysis of the video-PEEM images (upper inset). From [12].

transitions on specific domains or different ingredients, in the case of spatially separated active components.

3. Applications

Our particular interest was directed to kinetic instabilities in CO oxidation, such as catalytic ignition and extinction which occur under unsteady-state conditions and are important for catalytic treatment of automotive exhaust gases [14,15]. A specific applied problem is the so-called “cold-start”, where the effectivity of the catalytic converter remains very low until it warms up to the “ignition” temperature, at which the reaction rate rapidly switches from low to high conversion. Any method aiming an accelerated heating of the converter in order to quickly reach the critical temperature, such as operation at lean air-to-fuel ratio, exhaust system combustion devices, secondary air injection into the exhaust, electrically heated catalysts, causes additional energetic expenses [16]. Thus there is a substantial interest in studies of ignition–extinction processes which could promise an “energy-neutral” solution via lowering the critical temperature. In the case of CO oxidation, the sudden increase of the reaction rate at increasing temperature is related to the “kinetic

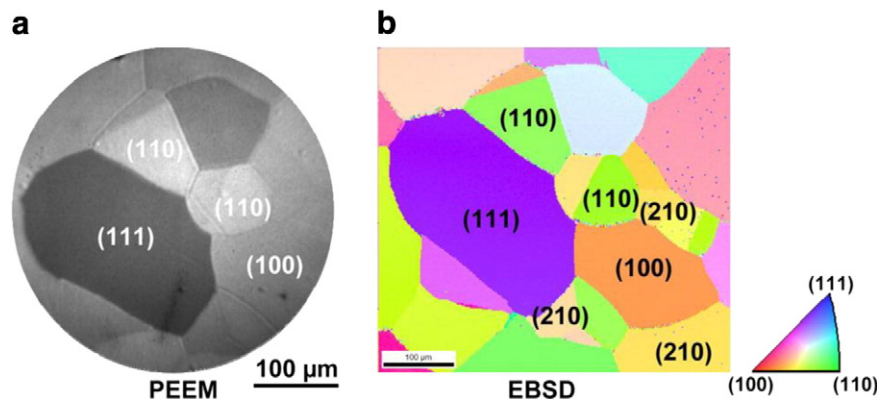


Fig. 1. An example of a polycrystalline Pt foil: a) as imaged in PEEM; and b) identification of individual surface domains by EBSD. Note the inverse pole figure assigning the corresponding directions. From [13].

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