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Generalised two-dimensional correlation analysis of the Co, Ce, and Pd mixed oxide catalytic systems for methane combustion using *in situ* infrared spectroscopy

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ABSTRACT

The process of methane combustion over the surface of a catalyst is still not fully understood. The identification of the reaction path and the intermediates created during catalysis is crucial for understanding the transformation of methane molecules. Two-dimensional (2D) correlation spectroscopy was engaged as a tool for the quantitative analysis of a series of temperature-dependent infrared spectra registered *in situ* during methane combustion. The prepared samples of catalysts were based on a Co, Pd and Ce mixed oxide adsorbed on an aluminium oxide layer deposited on kanthal steel. The registered spectra were transformed into 2D synchronous and asynchronous contour maps. The sequential order of spectral intensity changes was determined, and the resolution enhancement of overlapping IR bands by 2D correlation was demonstrated. The changes in the bands' intensity and information about band position can be correlated with a specific bond, and thus, the possible process intermediates can be identified. The 2DCoS analysis proved to be a powerful tool for band enhancement and revealed the changes occurring within the analysed catalyst systems as responses to increased temperature.

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1. Introduction

Two-dimensional (2D) correlation spectroscopy has gained much popularity among researchers within the last several decades, especially in the field of life science [1–3]. The mathematical transformation of the registered series of spectra (and other results like chromatographs *etc.*) can be presented in a wide variety of forms, but the most common are 2D synchronous and asynchronous contour maps [1,4]. The idea of two-dimensional correlation spectroscopy was developed and described by Noda [5], and further introduced to the broad range of techniques in 1989, as a form of generalised two-dimensional spectroscopy [4,6]. The 2D maps are generated as a result of the mathematical transformation details described in the literature [6,7] and have the specified properties and structure. Two parts of the spectra, synchronous and asynchronous, give complementary information about the process characteristics and variations. The synchronous part represents the simultaneous changes of the spectra intensity for the analysed series, while the asynchronous part gives information about sequential or subsequent changes in band intensity [7,8].

To apply the advantages of 2DCoS, an analysed system has to be perturbed with any kind of external non-periodic stimulus, such as temperature, pressure, concentration, *etc.* [7]. Selected benefits of employing 2D correlation spectroscopy are [9] the significant simplification of complicated spectra (especially those consisting of many overlapped bands), detecting differences between the intensity profiles and the establishment of a non-obvious correlation between bands, and determination of the sequence of events by observing the various factors of changes in spectral intensities. The first feature is connected with the enhancement of spectral resolution performed by spreading the existed bands over the second dimension during the creation of contour maps. Over the last few years, this type of mathematical transformation of the spectra has been employed to describe biological systems [9,10], examine polymer systems [2], sample differentiation [11], and describing the progress of chemical reactions [12]. The main feature of 2DCoS is that it can enhance and describe the characteristic sequence of spectral intensity changes that occur during experiments with controlled perturbation on which the analysed system is exposed. The sequence of band intensity changes on the perturbation axes is determined from the synchronous and asynchronous maps according to Noda's rules.

Methane combustion has been investigated vigorously by many researchers over the last decade [13–18]. However, the problem of C–H bond activation is the current topic in research [14,19,20]. In the

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literature, many descriptions and theories that involve the Langmuir-Hinshelwood, Mars-van Krevelen or Eley-Rideal mechanisms to explain the interaction between methane molecules and the active sites present on a catalyst surface can be found [21–23]. This only proves that the mechanism of catalytic combustion of hydrocarbons is unclear, and demands further investigation.

The last decade has also brought a relevant improvement in measurements obtained under conditions similar to the real systems, and thus expanded the applicability of vibration spectroscopy for monitoring the progress of the reaction. The catalyst's surface and its transformation with increased temperature, as well as the presence of methane molecules, are examined with *in situ* and *operando* spectroscopic methods [17,24–26]. Nowadays, those methods are considered as standard techniques for the surface analysis of catalysts. Additional methods that can extend their capabilities and simplify the analysis process (often involving very complex spectra) are desirable.

In this study, the *in situ* homospectral two-dimensional correlation spectroscopy was used to evaluate the catalytic combustion of methane over various Ce, Pd and Co mixed metal oxide structured catalysts in order to identify the surface intermediates that appear with increased combustion temperature, and propose the mechanism of the catalytic process.

2. Material and Methods

2.1. Preparation of Catalysts

The series of cobalt, cerium and palladium nanocomposite structured catalysts employed in this study was prepared by incipient wetness impregnation from nitrate solutions of a washcoated layer of γ -Al₂O₃ deposited on kanthal steel. A detailed description of the preparation procedure can be found in our previous study [27]. In brief, the experimental steps started with the calcination of stainless steel sheets (0.1 mm sheets, Goodfellow Cambridge Limited; composition: Fe: 72.8%, Cr: 22.0%, Al: 5.0% and Y: 0.1%, Zr: 0.1%) at 1000 °C for 24 h. That thermal treatment results in the creation of a thin adhesive alumina layer on the metal sheet surface, on which a further γ -Al₂O₃ washcoat layer can be anchored. The prepared sheets were then cut into pieces of 1.4 cm × 1.6 cm and used as a base for a washcoated layer of γ -Al₂O₃ by the Yoldas sol-gel method [28] based on a 30 wt% aluminium tri-sec butoxide solution (Sigma-Aldrich 97%, CAS No. 2269–22-9) and the dip-coating method with a withdrawal speed of 3 cm/min. These supports, after subsequent calcination at 500 °C for 6 h, were impregnated with the metal nitrate solutions as shown in Table 1. The sample name indicates the promotor metal used during catalyst impregnation. Then the catalysts were dried in ambient conditions and calcined at 500 °C for about 3 h. The metal content for the prepared catalysts were determined by X-ray Fluorescence Spectroscopy (XRF) as it was described in [29].

2.2. Spectra Collection

Spectra were collected with the THERMO/Nicolet 8700 spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector (for scanning in mid-IR range) and a Praying Mantis High-Temperature Reaction Chamber (Harrick Scientific Co., Ossining,

NY) with ZnSe windows. The entire optical path of the spectrometer and DRIFT instrument was purged with dry air to remove water vapour and carbon dioxide that would give their characteristic bands in the DRIFT spectrum and mask the corresponding spectral range. The registered spectra are based on the registration of diffuse reflected light that reaches the detector due to the ellipsoidal mirrors in the Praying Mantis DRIFT system after removing specular reflection. The MCT-A detector operates in the frequency range of 4000–650 cm⁻¹. The spectrum of each catalyst sample at a particular temperature was the result of 32 co-added scans with 4 cm⁻¹ spectral resolution. The instrument was controlled by OPUS v 8.0 software.

The temperature-dependent spectra were collected during two experimental procedures. In each procedure, the collection of the spectrum proceeded after stationary conditions were achieved in the reaction chamber in which the catalyst sample was placed. The following procedure includes increasing the temperature by 50 °C with a heating rate of 2 °C·min⁻¹. The first procedure can be described as dynamic experiments without oxidative gases. The catalyst samples were, after dehydration in a helium flow, examined for methane transformation at various temperatures (from ambient to 450 °C). In the following step, a mixture of 1.600 mol% CH₄/He (Air Products, calibration mixture, ±0.5% rel.) was inserted into the reaction chamber with a total flow of 25 cm³·min⁻¹ at 110 °C. Then the spectrum was collected and the temperature increased by 50 °C at a heating rate of 2 °C·min⁻¹. After every 50 °C, the spectrum was measured. The second procedure was similar, with the only exception being that the carrier gases consisted of 1.600 mol% CH₄/20.900%O₂/He (Air Products, calibration mixture, ±0.5% rel.). This change provided oxidative conditions within the reaction chamber.

2.3. Spectra Pre-Processing and Analysis

For the purposes of 2DCoS, collected data were pre-processed with baseline correction and normalisation. The described treatments were carried out in OriginPro software (OriginLab, OriginPro 9.2, USA) and using CHEMOFACE software [30].

The 2D correlation spectroscopy calculations were performed in 2D Shige software composed by Shigeaki Morita [31] (Department of Chemistry, Kwansei Gakuin University, Japan), based on the differential spectra. The results were plotted in Origin software as contour plots. The colour palette was selected in such a way that warm colours (yellow to red) corresponded to a positive value while cold colours (from green to blue) corresponded to a negative value.

The procedure of analysing of 2D correlation spectra according to the Noda's rules has been provided in the Supplementary material.

3. Results and Discussion

However, the general equation for the reaction of methane combustion can be presented as CH₄ + 2O₂ → CO₂ + 2H₂O, the reaction which occurs in industry processes which take place over the catalyst surface and involves many intermediate steps. The reaction takes place in a few milliseconds [32], nevertheless the exact mechanism is still not fully understood. The main molecules formed in the abatement of methane at relatively low temperature range (~300–450 °C) that are discussed in the literature are methyl alcohol, formaldehyde, formic acid, carbon monoxide, carbon dioxide and water. However the methyl alcohol, formaldehyde and formic acid molecules were detected only with usage of chromatography methods. Nowadays the research can be performed with *in situ* spectroscopy methods and the intermediates can be detected directly during the reaction. As it was discussed in the literature and proved by *in situ* experiments under real conditions [29] mentioned above molecules do not appear on the surface during the reaction. The *in situ* experiments proved that the formates and carbonates are intermediate products of methane oxidation. The further discussion on series of DRIFT spectra was to identify bands that behave in a similar

Table 1

The prepared catalysts nomenclature and the active metal content.

Catalyst name	Name of impregnation solution (impregnation order)	Metal content (%wt) determined by XRF [29]
Co/Pd/ γ -Al ₂ O ₃	Pd(NO ₃) ₂	Pd: 0.40 ± 0.06
	Co(NO ₃) ₂	Co: 31.1 ± 4.9
Ce/Co/ γ -Al ₂ O ₃	Ce(NO ₃) ₃	Ce: 0.98 ± 0.03
	Co(NO ₃) ₂	Co: 8.63 ± 0.29
Pd/ γ -Al ₂ O ₃	Pd(NO ₃) ₂	Pd: 17.0 ± 2.7

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