



Evolution of self-sustained kinetic oscillations in the catalytic oxidation of propane over a nickel foil



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ARTICLE INFO

Article history:

Received 23 July 2015

Revised 30 October 2015

Accepted 18 November 2015

Available online 17 December 2015

Keywords:

Heterogeneous catalysis

Propane oxidation

Nickel

Self-sustained rate oscillations

ABSTRACT

The evolution of self-sustained reaction-rate oscillations in the catalytic oxidation of propane over a nickel foil has been studied in situ using X-ray photoelectron spectroscopy coupled with online mass spectrometry and gas chromatography. Changes in the effective surface area and in the catalyst morphology under reaction conditions have been examined by scanning electron microscopy and a krypton adsorption technique. It is shown that the regular kinetic oscillations arise under oxygen-lean conditions. CO, CO₂, H₂, H₂O, and propylene are detected as products. The conversion of propane oscillates in a range from 1% to 23%. During the half-periods with high activity, the main reaction pathway is the partial oxidation of propane: selectivity toward CO achieves 98%. In contrast, during the half-periods with low activity, the reaction proceeds through three competitive pathways: the partial oxidation of propane, the total oxidation of propane, and the dehydrogenation of propane to propylene. The driving force for the self-sustained kinetic oscillations is the periodic reoxidation of nickel. According to the Ni2p and O1s core-level spectra measured in situ, the high-active catalyst surface is represented by metallic nickel, whereas during the inactive half-periods the catalyst surface is covered with a thick layer of NiO. The intensity of O1s spectra follows the oscillations of O₂ in the gas phase during the oxidation of propane. It is found that during the induction period before the regular oscillations appear, a rough and porous structure develops because of strong reconstruction of the catalyst surface. The thickness of the reconstructed layer is approximately 10–20 μm. This process is accompanied with at least an 80-fold increase in the effective surface area compared with a clean, non-treated nickel foil, which undoubtedly leads to a drastic increase in the number of active sites. We believe that it is the main reason for the induction period always being observed before the appearance of self-sustained oscillations in the catalytic oxidation of light hydrocarbons over catalysts with a low specific surface area (single crystals, foils, or wires). Moreover, without such reconstruction, the oscillations cannot arise due to low activity of such catalysts.

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1. Introduction

Nonlinear behavior, such as self-sustained reaction-rate oscillations, is a widespread phenomenon in heterogeneous catalysis. To date the self-sustained kinetic oscillations have been observed in approximately 40 catalytic reactions in a wide pressure range from ultrahigh vacuum up to atmospheric pressure over

all types of catalysts including single crystals, polycrystalline foils, wires, foams, and supported catalysts. [1–4]. A wide class of these reactions is the oxidation of hydrocarbons over transition metals. For instance, self-sustained rate oscillations have been noted in the oxidation of methane, ethane, propane, and butane over supported and unsupported catalysts based on Ni, Co, Pd, Pt, Rh, and Ru [5–24]. The distinctive features of these oscillations are their long periods, ranging from several seconds to tens of minutes, and an induction period before the appearance of the regular oscillations. These oscillations arise under oxygen-lean conditions.

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For instance, the oscillations in the oxidation of propane over Ni exist when the propane/oxygen molar ratio ranges from 3/1 to 15/1 [25]. Besides, strong reaction-induced changes in the catalyst morphology are observed during the oscillations [11,15,23].

It is generally thought that these oscillations arise from repetitive cycles of oxidation and reduction of the metal surface, and the detailed nature of the oscillations depends on the relative activities of the oxidized and reduced surfaces. Recently, it has been confirmed directly by the results of in situ studies [25–27]. However, the reasons that initiate the appearance of these oscillations are not clear yet. The aim of the present work was to investigate in detail the evolution of self-sustained rate oscillations in the oxidation of propane over nickel. Earlier, it was found that the regular oscillations in this catalytic system appear at a pressure of about 1 mbar [23]. It allowed us to apply surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS) coupled with online mass spectrometry (MS) and gas chromatography (GC) for the in situ study of this phenomenon [25]. XPS is a powerful tool of the heterogeneous catalysis to investigate both the surface composition and the nature of adsorbed species, while mass spectrometry can provide the abundance of products and reactants in the gas phase [28,29]. The usage of gas chromatography allows us to measure the conversion of reagents and selectivity toward the main reaction products during the oscillations. Also, the effective surface area and the morphology of nickel foils used as the catalyst were examined by scanning electron microscopy (SEM) and a krypton adsorption technique before and after the appearance of the regular oscillations.

2. Experimental section

The in situ experiments were performed at the Innovative Station for In Situ Spectroscopy (ISIS) beamline at the synchrotron radiation facility BESSY II (Berlin, Germany). The experimental station was described in detail elsewhere [29]. In short, this station is equipped with an electron energy analyzer PHOIBOS-150 (SPECS Surface Nano Analysis GmbH), a gas cell, and a system of electron lenses. The lens system was combined with three differential pumping stages that provided UHV conditions in the electron energy analyzer even when the pressure in the gas cell reached 10 mbar. The high brilliance of the synchrotron radiation combined with a short travel length of the photoelectrons through a “high-pressure” zone in the gas cell allowed us to obtain high-quality core-level spectra under flow conditions with time resolution of approximately 100 s.

In all the experiments, rectangular pieces of a 0.125 mm thick nickel foil (purity 99.99%, Advent Research Materials Ltd.) were used as the catalyst. In the XPS experiments, a sample 9×9 mm in size was mounted on a sapphire sample holder between a SiC plate and a stainless steel plate, which had a hole of 8 mm in diameter for measuring the core-level spectra of the catalyst surface. The sample was heated from the rear via the SiC plate with a NIR semiconductor laser ($\lambda = 808$ nm). This system allowed us to heat the sample up to 1000 °C in vacuum. The sample temperature was monitored with a K-type thermocouple spot-welded directly to the foil edge. The station was also equipped by an extractor type ion source operated at 10^{-4} mbar of argon, which can be used for cleaning the surface of samples under study.

The propane and oxygen flows were regulated separately with mass-flow controllers (Bronkhorst High-Tech BV). The total pressure of the reactant mixture in the gas cell was measured with a MKS type 121A baratron (MKS Instruments Inc.). During the experiments, the total pressure in the gas cell was kept at a constant level of 0.5 mbar using a special automatic pumping system [29]. The gas-phase composition was monitored continuously with an online quadrupole mass spectrometer Prizma QMS-200 (Pfeiffer

Vacuum GmbH) connected through a leak valve to the gas cell. The GC analysis was made using an online four-channel micro gas chromatograph CP-4900 (Varian Inc.) equipped with thermal conductivity detectors. Because the gas chromatograph can sample gas mixtures only at atmospheric pressure, in our experiments the sampling was performed in the outlet of the automatic pumping system consisted of a turbo pump ventilated by dry N_2 and coupled with a membrane pump which provided the compression of the gas mixture from 0.5 mbar to 1 bar. Before the experiments, the gas chromatograph was calibrated with respect to propane, oxygen, and the main reaction products: C_3H_6 , CO, CO_2 , H_2 , and H_2O . The selectivity (S_i) toward a product i (propylene, CO, or CO_2) was calculated using the partial pressures of products (p_i) determined by GC and inverse values of the stoichiometric coefficients (k_i) according to a formula as follows:

$$S_i = k_i \times p_i / \sum (k_j \times p_j) \times 100\%,$$

where $k_i = 1/3$ for CO and CO_2 , and $k_i = 1$ for C_3H_6 .

All the photoelectron spectra were collected at the normal emission at the constant pass energy of 10 eV; their intensities were normalized to the ring current. The $Ni2p_{3/2}$, $O1s$, and $C1s$ core-level spectra were obtained with photon energies of 1050, 730, and 485 eV, respectively, that provided the same kinetic energy (approximately 200 eV) for each region and, correspondingly, the same analysis depth of approximately 1.7 nm. In all cases, the valence-band spectra were acquired at the same photon energy as an adjustable spectrum. The positions of the photoelectron peaks on the binding energy scale were referenced to the Fermi edge of nickel in the metallic state.

All spectra were analyzed using the CasaXPS software [30]. A Shirley-type background was subtracted from each spectrum. The line shape used for fitting the $Ni2p_{3/2}$ spectra of nickel in the oxidized state and the $O1s$ spectra was the product of Lorentzian and Gaussian functions. An asymmetric, so-called LF [30] line shape was used for approximation of the $Ni2p_{3/2}$ spectra of nickel in the metallic state. Note that the asymptotic form of the LF line shape is equivalent to the asymptotic form of the theoretical Doniach–Sunjic asymmetric line shape. However, this new line shape describes the asymmetric XPS peak more correctly than the conventional Doniach–Sunjic function does because the LF function is finite. The parameters of all peaks observed in the $Ni2p_{3/2}$ and $O1s$ spectra are summarized in Supporting information, Table S1.

The effective surface area and the morphology of nickel foils before and after the appearance of the regular oscillations were examined using scanning electron microscopy and a gas adsorption technique. The catalytic testing of these foils was performed on a flow reactor equipped with a quadrupole mass spectrometer (see details elsewhere [22,23]). Because the effective surface area of the samples was extremely small, we used Kr adsorption at 77 K, which is a much more sensitive technique compared to conventional methods based on N_2 and Ar adsorption. Isotherms of krypton adsorption were measured using an adsorption analyzer ASAP 2010 (Micromeritics Instrument Corp.). The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The cross-section area of Kr molecules was assumed to be equal to 21.0 \AA^2 . Before measurements, all the samples were degassed at 200 °C in vacuum for 1.5 h. The surface morphology was studied using a scanning electron microscope LEO 1430 (Carl Zeiss) and a focused ion beam (FIB) system Crossbeam 1540XB (Carl Zeiss). Surface profiling measurements were performed using a FIB “lift-out” technique for the cross section preparation of the sample under study [31]. For this purpose, a rectangular pit in a nickel foil was milled using a focused Ga^+ ion beam. Then the sample was tilted to a steep angle (54°), and SEM images of a sidewall of the pit were obtained.

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