

# Oscillations of partial oxidation of methane over H-ZSM-5 supported rhodium catalyst

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## Abstract

A Rh/H-ZSM-5 catalyst has been found to catalyse the partial oxidation of methane at atmospheric pressure, and regular oscillations in both reactants and products have been observed. Temperature-programmed techniques, such as TPD, TPO and TPR, were performed to look into the reaction mechanism. The oscillatory behavior may be attributed to the synergism of the formate species and the oxide with certain interaction with the support.

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## 1. Introduction

Revelation of regimes of oscillatory behavior in catalytic processes may lead to new insights into the reaction mechanisms and achieve a better understanding of the operation and improvement of the practical catalysts [1]. Studying this behavior can provide information which could not be extracted from the analysis in the nonoscillatory mode [2]. The oscillatory behavior during the catalytic oxidation/combustion of methane over the supported and unsupported nickel [3–8] and palladium [9–13] catalysts has been the subject of considerable number of recent publications. However, the oscillatory mechanism is still not understood in detail, although it is generally accepted that the cyclic oxidation/reduction process is responsible for the oscillation.

Ruckenstein and Hu [3] were the first who observed catalyst temperature oscillation during partial oxidation of methane over supported nickel catalyst. They considered that

the hot spots on the Ni/SiO<sub>2</sub> catalyst moving up and down caused the oscillation of the catalyst temperature, and were probably due to the reduction and oxidation of the catalyst by the reactants. But no oscillations were detected in the product concentrations. In a series of studies conducted by Zhang et al. [6–8,14] in the partial oxidation of methane (POM) reaction, the oscillations were observed in terms of reactant and product concentrations, as well as temperatures, and in general, maxima in the product oscillations of CO<sub>2</sub> and CO (H<sub>2</sub>) corresponded to minima in the CH<sub>4</sub> and O<sub>2</sub> reactant oscillations. The results obtained from the experiments indicated that methane oxidation was related to the behavior of the catalyst surface switching back and forth from the reduced state to the oxidized state.

In this paper, we report the first observation of oscillations over Rh/H-ZSM-5 catalyst with certain SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio when an argon/methane/oxygen mixture was passed, and the further investigations into the oscillatory reaction kinetics. The oscillations were studied in terms of reactant and product concentrations. By varying the reaction conditions, the regime of oscillatory behavior has been changed, which could lead to new insights into the oscillation mechanism.

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## 2. Experimental

### 2.1. Materials

The catalysts were prepared by impregnating H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$  and 50, nominated as H25 and H50, BET surface area 329 and 301  $\text{m}^2/\text{g}$ , Nankai University) with an aqueous solution of  $\text{Rh}(\text{NO}_3)_3$  in order to have a final Rh loading of 1 wt.%. The support H-ZSM-5 is precalcined in the muffle at 800 °C for 4 h. After impregnation, the samples were dried and then calcined at 800 °C for 4 h, giving the catalysts designated as fresh. The resultant catalysts for the test were crushed and sieved. Rh supported on  $\text{SiO}_2$  (BET surface area 230  $\text{m}^2/\text{g}$ , Aldrich) and  $\gamma\text{-Al}_2\text{O}_3$  (BET surface area 145  $\text{m}^2/\text{g}$ , Alfa) samples were prepared with the same method for comparison.

The structure and the composition of the catalysts were determined by the X-ray diffraction using Rigaku Dmax/RC instrument with the Cu  $K\alpha$  radiation at 40 kV and 30 mA. It was observed, from the X-ray diffraction patterns of the Rh/H-ZSM-5 catalysts obtained before and after reaction, that the samples submitted to the reaction conditions shows the lowest intensity of the high miller index diffraction peaks of the zeolite, meaning a partial destruction of the zeolite matrix. No Rh-based phases are detected by XRD due to low metal loading (1 wt.%).

### 2.2. Apparatus and procedure

The temperature-programmed tests were carried out in a fixed bed quartz reactor connected to a quadruple mass spectrometer (Baltzers QMS 2000) at atmospheric pressure. The amount of catalyst was 40 mg. The reactor was inserted into an oven, and the temperature was controlled by ÜGU-AI-708 controller. The temperature was measured by a K-type thermocouple. The reactant mixture, consisting of a pre-mixed gas ( $\text{CH}_4:\text{O}_2:\text{Ar} = 2:1:45$ ), was introduced in the reactor with a total flow rate of 10 ml/min in the TPSR (temperature-programmed surface reaction) experiment. The temperature increased at 15 K/min till the required point, and that is for all experiments.

The reduction of the catalysts were performed by heating the sample from RT to 800 °C in 5%  $\text{H}_2/\text{Ar}$  with the flowrate 10 ml/min. The reoxidation of the catalysts and identification of coke on the catalysts were measured by oxidation in 20%  $\text{O}_2/\text{He}$  (20 ml/min). TPD experiments were carried out in the pure helium flow (20 ml/min).

## 3. Results

### 3.1. Oscillatory behavior of the Rh/H50 catalyst in $\text{CH}_4\text{-O}_2\text{-Ar}$ mixtures and the influence of temperature

The occurrence of the oscillations during the POM reaction was observed by studying the catalytic behavior of the

fresh catalysts samples in their TPSR experiments, as shown in Fig. 1. It should be noted that the QMS signal of both the reactants and products illustrated in the figures have been vertically offset by the factors shown in the figures. Oscillations were observed for the Rh/H50 catalyst. The typical oscillation patterns displayed during the partial oxidation of methane for Rh/H50 at low and high temperatures are depicted in Fig. 2. The frequency was found to be dependent on the temperature. The increase in the frequency of the oscillation with rising temperature is due to the increase in the transformation rate of the chemical state of catalytic surface. Fig. 3 shows two complete oscillation cycles of Fig. 2c. It can be seen that CO and  $\text{H}_2$  oscillated with the minimum production corresponding to the  $\text{CO}_2$  peak in production. Maxima in the product oscillations of CO correspond to minima in the  $\text{CH}_4$  reactant oscillation, and there is an appreciable hysteresis in the peak of  $\text{H}_2$ . These phenomenon are quite different from Zhang's description in their articles. It can also be seen that the oxygen signal is always close to zero, showing that virtually all of the oxygen was used up in the reactions and oscillations. Thus, the rate of oxygen uptake remained constant, even though the production of oxygen containing products fluctuated wildly. This observation can only be explained if the oxygen was alternatively stored and then released from the surface. On this basis, the sharp peaks can be associated with the rapid reduction of rhodium oxide and the long tail that follows with the re-oxidation of the surface. That would be discussed in detail later.

### 3.2. The effects of catalyst pretreatment

To obtain information on the influence of catalyst pretreatment on the occurrence of oscillations, tests were made in which the catalyst was preheated using different feed compositions. The results of the activity in POM after the introduction of the reaction mixtures are shown in Fig. 4 for three different types of pretreatment to 800 °C: (i) in a feed of 20%  $\text{O}_2/\text{He}$ , (ii) in a feed of 5%  $\text{H}_2/\text{Ar}$ , and (iii) in a feed of pure helium.

In the case of the pretreatment in the oxidation gas mixture, the reaction exhibited more regular oscillatory behavior than that over the fresh catalyst (Fig. 4a). The TPSR profiles obtained for the Rh/H50 catalyst after preheated in the 5%  $\text{H}_2/\text{Ar}$ , as shown in Fig. 4b, the induction time before oscillations was shortened. In the case of pretreatment in helium only, the performance of the reaction was stable and high (Fig. 4c). This data clearly show that helium in the feed determines a complete change in the dynamic reactivity characteristics of the catalyst.

To obtain further information on the role of rhodium oxide species in changing catalyst reactivity, a different type of experiment was carried out. In these tests, the same pretreatment to 800 °C in the reduction and helium flow was made, but after the reactor was cooled to RT, the catalyst was further pretreated using 20%  $\text{O}_2/\text{He}$  heated up to 800 °C. Oscillations were not observed on the reduced/re-oxidation samples, as

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