

# Vanadium species in new catalysts for the selective oxidation of methane to formaldehyde: Activation of the catalytic sites

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## Abstract

New vanadium oxide supported on mesoporous silica catalysts for the oxidation of methane to formaldehyde were investigated by infrared and Raman spectroscopies to identify and characterize the molecular structure of the most active and selective catalytic sites. *In situ* and operando experiments have been conducted in order to understand the redox and hydroxylation/dehydroxylation processes of the vanadium species. (SiO)<sub>2</sub>VO(OH) species were identified in these catalysts in reaction conditions and shown to undergo a deprotonation at 580 °C under vacuum, leading to a site giving a photoluminescence band at 550 nm attributed to reverse radiative decay from the excited triplet state:

$(V^{4+}-O^-)^* \rightleftharpoons (V^{5+}=O^{2-})$ . An activation mechanism of vanadium monomeric species with electrophilic oxygen species is proposed.

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## 1. Introduction

In the past decade, considerable interest has been shown in developing a process to selectively oxidize methane to formaldehyde or methanol. The challenge facing by the scientists is particularly difficult because of the low reactivity of the starting alkane molecule. However, progress has been made with catalysts corresponding to vanadium oxide supported on silica which are currently the best performing catalysts for the oxidation of methane to formaldehyde [1–5].

Recently, we reported better performances of new catalysts based on vanadium oxide supported on mesoporous silica for partial oxidation of methane to formaldehyde [6]. These catalysts were prepared using a new method based on the co-condensation of vanadium and silica precursor species at neutral pH in a

solution containing a template [7]. We confirmed the importance of isolation of the vanadium sites since a higher quantity of vanadium monomeric species was obtained with this method as deduced from TPR curves [6,8]. The presence of two types of monomeric species on the dehydrated surface of our catalysts was also highlighted from Raman and IR experiments [6,8]: these species would correspond to two types of V<sup>5+</sup> cations (i) with one V=O bond and three bridging V–O–Si bonds and (ii) with one V=O bond, two bridging V–O–Si bonds and one V–OH group. Hydroxylated monomeric species were characterized by an IR band at 3656 cm<sup>-1</sup> attributed to the  $\nu(\text{VO-H})$  stretching vibrations, the intensity of which increased with the vanadium content [6,8]. Additionally, it was shown that our preparation method favoured the formation of a higher amount of D2 defects and hydroxylated monomeric species by comparison with a reference V/MCM41 catalyst. It was proposed that the hydrolyzed D2 silica defects could be the preferential anchoring sites for these species [8]. Hydroxylated monomeric species stabilized at the surface of the catalysts around 600 °C would be the most efficient methane oxidation sites explaining the better catalytic activities of the described catalysts.

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In this study, in order to explain the better catalytic properties, we have conducted spectroscopic characterization by IR and Raman spectroscopies focused on the vanadium molecular structure and the other surface species as well as when the catalysts were submitted to various redox treatments at the catalytic reaction temperature under vacuum or directly under reaction conditions with a simultaneous collection of catalytic data by mass spectrometry (operando methodology). In addition to the operando Raman experiments, the characterization of vanadium species after soft reducing treatments was achieved to investigate the redox cycle.

## 2. Experimental

Vanadium oxide supported on mesoporous silica catalysts have been prepared as described previously [6–8]. A solution containing  $\text{NH}_4\text{VO}_3$  and cetyltrimethylammonium bromide ( $\text{C}_{16}\text{TMABr}$ ) with  $\text{NH}_4\text{Cl}$  (used as a buffer) was first prepared. The pH value of the solution was 5–6 before tetraethoxysilicate (TEOS) was added. The molar proportions of precursors were similar for all the samples ( $\text{TEOS}/\text{NH}_4\text{Cl}/\text{C}_{16}\text{TMABr}/\text{H}_2\text{O} = 0.5/9.2/0.12/130$ ) and only the  $\text{NH}_4\text{VO}_3$  proportion was varied. After a reflux of the solution for 24 h at 40 °C, the precipitate was filtered and washed with hot water. The template was extracted by washing with ethanol at 80 °C for 2 h. After drying at 100 °C for 12 h, the compound was calcined at 650 °C for 6 h in air flowing at 50 ml  $\text{min}^{-1}$ . Two samples have been prepared with this method using  $\text{NH}_4\text{VO}_3$  molar proportions of 0.012 and 20 and characterized in this study. They contained respectively 2.1 and 3.5 wt.% of V and were named 2.1%V/mesoSiO<sub>2</sub> and 3.5%V/mesoSiO<sub>2</sub>.

The Raman study was achieved using the violet exciting line at 458 nm of a 2018 RM Ar<sup>+</sup>–Kr<sup>+</sup> laser (Spectra physics). The spectra of samples were recorded with a UV–vis–NIR LabRam HR Raman spectrometer (Horiba–Jobin Yvon) equipped with a confocal microscope, Notch filter and CCD detector. The diffused light was spatially dispersed with a 1800 grooves/mm or a 300 grooves/mm diffraction grating. A long working distance objective ( $\times 50$ ) allowed focusing of laser and collection of retro-diffused light in the cells. The laser power on the samples was typically 2 mW, conditions under which no significant laser heating was observed.

Raman spectra were collected during methane oxidation to formaldehyde in the 150–4000  $\text{cm}^{-1}$  spectral region. The Raman setup allowing recording spectra of working catalysts is described in Fig. 1. It consists of a homemade furnace containing heating plugs and a specially designed quartz reactor containing a quartz window for light transmission, thermocouple hollow, and inlet–outlet gas connections. The 2.1%V/mesoSiO<sub>2</sub> and 3.5%V/mesoSiO<sub>2</sub> samples were studied by operando Raman. The quality of spectra was poorer for 2.1%V/mesoSiO<sub>2</sub> because of its lower V content and hence only spectra of 3.5%V/mesoSiO<sub>2</sub> are presented in this article. For the operando study, 110 mg of the catalyst were placed in the quartz reactor, which reactor was then introduced into the complementary space of the furnace allowing its support and good thermal exchanges. A thermal screen was finally added to

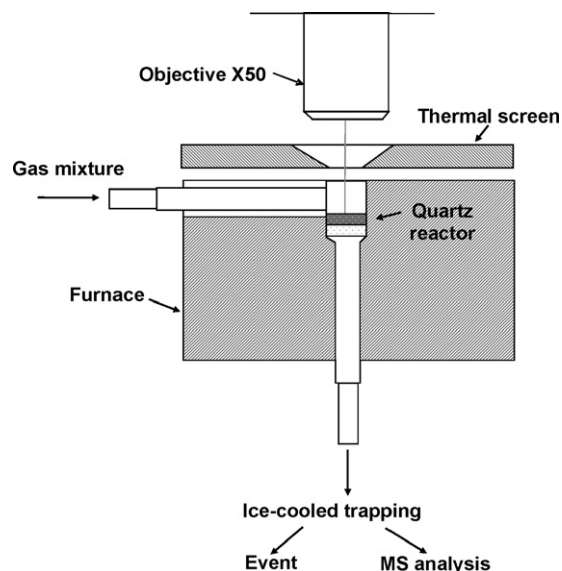


Fig. 1. Schematic representation of the operando Raman cell.

protect the objective. The reaction temperature was varied from 540 to 600 °C under a 90 ml  $\text{min}^{-1}$  reaction gas flow at atmospheric pressure. The feedstock composition was 40%N<sub>2</sub>/13%O<sub>2</sub>/38%CH<sub>4</sub>/9%H<sub>2</sub>O. Steam was obtained using a saturator and the condensable products were trapped in water cooled with ice, and formaldehyde was chemically analysed as described previously [6]. CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, CO and CO<sub>2</sub> were analysed on-line by a VG ProLab mass spectrometer (Thermo Electron Corporation). No other gas was detected by mass spectrometry. Conversion of methane was determined by following variation of mass 15. A treatment cell with two valves and a quartz window was also used to achieve Raman spectra of powders after treatments at 580 °C under vacuum of  $2 \times 10^{-5}$  mbar or under pure oxygen flow.

Self-supporting disks (about 10 mg  $\text{cm}^{-2}$ ) were prepared by pressing the synthesized samples at 4 bar. They were treated at 580 °C in a homemade infrared cell either under pure O<sub>2</sub> flow at atmospheric pressure, under a vacuum of  $2 \times 10^{-5}$  mbar or under a 40%N<sub>2</sub>/13%O<sub>2</sub>/38%CH<sub>4</sub>/9%H<sub>2</sub>O gas mixture at 550 °C at atmospheric pressure. After treatments, the IR spectra were recorded at room temperature with a Fourier transform Vector 22 (Brüker) spectrometer.

EPR has been used for monitoring the generation of O<sup>-</sup> radical anions on 2.1%V/mesoSiO<sub>2</sub>. The results were compared with a conventional 1.7%V/SiO<sub>2</sub> catalyst studied in detail previously [9]. The concentration of oxygen radical anions (O<sup>-</sup>, O<sub>2</sub><sup>-</sup>) formed after re-oxidation of reduced catalysts was measured. An ERS-221 spectrometer was used for registration of X-band ESR spectra at variable temperatures. A homemade computer programme (EPR-CAD) was used for processing the experimental data. The samples were placed into quartz ampoules and subjected to standard pretreatment that included several cycles of heat treatment (500 °C) in oxygen (10 Torr) and under vacuum ( $10^{-6}$  Torr). This treatment is similar to the sample pretreatment traditionally used by us in experiments performed *in situ* [10,11]. It provides comprehensive cleaning of the surface from adsorbed organic impurities, water and carbon

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