



# Influence of gelation and calcination temperature on the structure-performance of porous VO<sub>x</sub>-SiO<sub>2</sub> solids in non-oxidative propane dehydrogenation



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## ABSTRACT

VO<sub>x</sub>-doped porous SiO<sub>2</sub> solids (VO<sub>x</sub>-SiO<sub>2</sub>) were synthesized at different gelation and calcination temperatures through an *in-situ* one-step synthesis and evaluated by non-oxidative propane dehydrogenation (PDH), exhibiting excellent catalytic performance. VO<sub>x</sub>-SiO<sub>2</sub> catalysts were characterized by XRD, low-temperature N<sub>2</sub> adsorption/desorption, SEM, TEM, UV-Vis, Raman, XPS, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR, and TGA. The structural and performance results for the catalysts reveal that gelation temperature has only a slight effect on the surface acidity, textural properties and VO<sub>x</sub> species dispersion of VO<sub>x</sub>-SiO<sub>2</sub> catalysts within a reasonable temperature range (30–60 °C). The 60-VO<sub>x</sub>-SiO<sub>2</sub>-580 catalyst, with a gelation temperature of 60 °C, a calcination temperature of 580 °C, and prepared by the one-step synthesis method, obviously shortens gelation process time by half compared to catalyst gelled at 30 °C and exhibits superior catalytic performance for PDH. Over high gelation temperature (≥75 °C) leads to the loss of integrity and decreases catalytic activity of the VO<sub>x</sub>-SiO<sub>2</sub> catalysts. Compared with the VO<sub>x</sub>-MCM-41 catalyst prepared by a one-step hydrothermal method, VO<sub>x</sub>-SiO<sub>2</sub> catalysts exhibit better catalytic activity and stability. Importantly, at a reaction temperature of 580 °C, the 60-VO<sub>x</sub>-SiO<sub>2</sub>-580 catalyst exhibits remarkable long-term catalytic stability in the eight reaction-regeneration cycles for PDH. Its propane conversion shows a slow decrease from 55% to 45% for a 4 h reaction duration, but the propene selectivity remains at approximately 91%. The results of this work will be beneficial for further industrial development and application of porous VO<sub>x</sub>-SiO<sub>2</sub> solids in catalysis.

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## 1. Introduction

Lower olefins are essential petrochemical intermediates, especially propene, which is widely used as a feedstock in the production of a variety of chemicals. Propene is mainly produced by steam cracking and fluid catalytic cracking (FCC) [1–4]. Besides these two approaches, catalytic dehydrogenation (DH) is an attractive alternative with the rapidly growing demand for propene and its derivatives [5–8]. DH processes can be classified into non-oxidative dehydrogenation and oxidative dehydrogenation of propane (ODHP). Although the latter (ODHP) has many advantages, such as avoiding thermodynamic equilibrium limitations and decreasing carbon deposition, the ODHP process unavoidably generates by-products due to deep oxidation of propene [9,10]. Non-

oxidative propane dehydrogenation (PDH) has been realized in commercial applications, where Pt- and Cr-based catalysts are frequently used [11,12]. Given the price and deactivation disadvantages of both catalysts, especially the pollution problem associated with CrO<sub>x</sub> species, current research tends to investigate novel catalysts for DH, such as V-, Ga-, and Sn-based catalysts [13–15].

V-based catalysts, which are one of the potential alternatives to Pt- and Cr-based catalysts for commercial PDH [16], are reasonably priced and environmentally friendly. In previous studies, these catalysts have been used mainly in oxidative dehydrogenation reactions [17–22]. Moreover, catalyst performance was strongly affected when different supports, such as SiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, were used [23,24]. To the authors' knowledge, the use of Al<sub>2</sub>O<sub>3</sub> and MCM-41 supports have been reported for V-based catalysts, which exhibit attractive catalytic properties for PDH [23,25–28]. Bai et al. investigated the catalytic performance and surface chemistry of mesoporous γ-Al<sub>2</sub>O<sub>3</sub> supported V-based catalysts, where

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the catalysts achieved high catalytic activity and superior stability [27]. Sokolov et al. systematically studied coke formation and catalyst stability for  $\text{VO}_x/\text{MCM-41}$ ,  $\text{VO}_x/\text{SiO}_2\text{-Al}_2\text{O}_3$ , and  $\text{VO}_x/\text{Al}_2\text{O}_3$  catalysts on PDH. By comparing the regeneration performance of V-, Cr-, and Pt-based catalysts, they found that the catalytic properties of the  $\text{VO}_x/\text{MCM-41}$  catalyst were stable for PDH in the absence of gas-phase  $\text{O}_2$  and could be fully recovered with oxidative regeneration. This full recovery was attributed to the high stability of  $\text{VO}_x$  species [23,25,26]. Rodemerck et al. also reported a relationship between catalyst deactivation and the  $\text{VO}_x$  species in the  $\text{VO}_x/\text{MCM-41}$  catalyst, where the catalyst shows superior catalytic properties for PDH [28]. Hence, it can be concluded that V-based catalysts could be a suitable candidate for a commercial PDH process.

A mesoporous silica monolith has been reported and possesses superior textural properties, but needs a lengthy gelation period at room temperature (at least six weeks) [29,30]. Fortunately, Yang et al. shortened the solvent evaporation process by using a liquid-paraffin medium to seal the ethanol solution, meaning that the prepared silica monolith can exactly copy the shape of the reactor [31]. They also proposed a one-step method to synthesize silica monoliths by doping various nanocrystals and found that the prepared materials had potential catalytic applications, but that vanadium species were not included [32].

Taking inspiration from the preparation and applications of mesoporous silica monoliths, the authors have prepared vanadium-doped porous silica solids ( $\text{VO}_x\text{-SiO}_2$ ) by a one-step synthesis in this study. The preparation method is environmentally-friendly, without loss of the  $\text{VO}_x$  precursor. The influence of gelation and calcination temperatures on the properties and catalytic performance of  $\text{VO}_x\text{-SiO}_2$  catalysts for PDH reaction was studied in detail. The prepared  $\text{VO}_x\text{-SiO}_2$  catalysts were characterized using a variety of state-of-the-art techniques and evaluated by a non-oxidative propane dehydrogenation reaction.

## 2. Experimental

### 2.1. Preparation of porous $\text{VO}_x\text{-SiO}_2$ solids

Porous  $\text{VO}_x\text{-SiO}_2$  solids were prepared by an *in-situ* one-step synthesis [32]. Catalyst preparation was performed as follows.  $\text{NH}_4\text{VO}_3$  (0.14 g, 99.95%, Aladdin) was dissolved in ethanol (10.00 g, Shanghai Chemical Agent Co. Ltd (China)) under mechanical stirring. Subsequently, anhydrous oxalic acid (0.14 g, 98%, Aladdin) was added to promote dissolution of  $\text{NH}_4\text{VO}_3$ , and the mixed solutions were stirred for 30 min at 40 °C. When the mixture was cooled to room temperature, 2.00 g of triblock copolymers P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , average Mn = 5800, Aladdin) was added and stirred until well mixed; 4.32 g of TEOS (tetraethoxysilane, 99.99%, Aladdin) and 0.40 g of aqueous HCl solution (0.8 M, Shanghai Chemical Agent Co. Ltd (China)) were slowly dripped into the mixture and stirred to dissolve them completely. Then the pellicular solution was poured into a porcelain crucible and heated under different temperatures (30 °C, 45 °C, 60 °C, 75 °C, and 90 °C) to form a silica gel. The prepared gel was sealed by a liquid-paraffin medium (Aladdin) and heated at 60 °C for 18 h to remove most of the ethanol and to form a rigid silica solid. Afterwards, the liquid-paraffin was captured on filter paper and collected for reuse. Finally, the obtained materials were calcined at 580 °C for 6 h under air atmosphere to remove P123 from the silica solids. The resulting catalysts of porous  $\text{VO}_x\text{-SiO}_2$  solids ( $\text{VO}_x\text{-SiO}_2$ ) with different gelation temperatures (recorded as GT- $\text{VO}_x\text{-SiO}_2\text{-580}$ ) denoted as 30- $\text{VO}_x\text{-SiO}_2\text{-580}$ , 45- $\text{VO}_x\text{-SiO}_2\text{-580}$ , 60- $\text{VO}_x\text{-SiO}_2\text{-580}$ , 75- $\text{VO}_x\text{-SiO}_2\text{-580}$ , and 90- $\text{VO}_x\text{-SiO}_2\text{-580}$ , respectively, where the content of doping V is 5 wt%. Before the catalytic test, the catalysts

were crushed and then tested in powder form due to the limits of the actual PDH reactor (8 mm inner diameter). As gelation temperature increased, the gelation process time gradually became shorter, as shown in Fig. 1. By the same preparation process, pure silica solid ( $\text{SiO}_2$ ) was synthesized at a gelation temperature of 30 °C and a calcination temperature of 580 °C. In addition, the catalysts with a gelation temperature of 60 °C were calcined at temperatures (recorded as 60- $\text{VO}_x\text{-SiO}_2\text{-CT}$ ) of 550 °C, 580 °C, 620 °C, and 650 °C. These catalysts were denoted as 60- $\text{VO}_x\text{-SiO}_2\text{-550}$ , 60- $\text{VO}_x\text{-SiO}_2\text{-580}$ , 60- $\text{VO}_x\text{-SiO}_2\text{-620}$ , and 60- $\text{VO}_x\text{-SiO}_2\text{-650}$ , respectively.

For comparison,  $\text{VO}_x\text{-MCM-41}$  was also synthesized by a one-step hydrothermal method. A certain amount of  $\text{NH}_4\text{VO}_3$  was dissolved in deionized water (10.0 g) under mechanical stirring to dissolve it completely. CTAB (1.7 g) and NaOH (0.27 g) were dissolved in deionized water (100.0 g) as a template solution. The  $\text{NH}_4\text{VO}_3$  solution was added to the template solution under mechanical stirring for 30 min. Then TEOS (10.5 g) was added dropwise to the mixed solution under stirring at 60 °C for 4 h. The synthesized gel was cooled overnight. Afterwards, it was transferred into a Teflon-lined autoclave and aged at 120 °C for 48 h. The obtained materials were washed five times with deionized water (750 ml) and dried at 60 °C for 12 h. Finally, it was calcined at 550 °C for 4 h to form a V-MCM-41 sample, where the content of V is 5 wt% according to the ICP result.

### 2.2. Characterizations

X-ray diffraction (XRD) analysis was collected on a Bragg-Brentano diffractometer (monochromatic Cu  $K\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ). The catalysts were scanned from 10° to 70° (2 $\theta$  value) using a scan speed of 5°/min at 40 kV and 30 mA. The vanadium and silicon contents of the catalysts were obtained with inductively coupled plasma atomic emission spectroscopy (ICP-AES) with Varian Vista MPX. Low-temperature  $\text{N}_2$  adsorption/desorption isotherms were measured using a NOVA4000 analyzer (Quantachrome, USA) at 77 K. Before analysis, the catalysts were degassed under vacuum at 300 °C for 4 h. The multipoint BET method was utilized to calculate the surface areas. The pore volumes of the catalysts were obtained at the maximum relative pressure ( $P/P_0$ ). The pore size distributions of the catalysts were derived from the desorption branch of the isotherms using the BJH model. For micropore analysis, the pore volume and pore

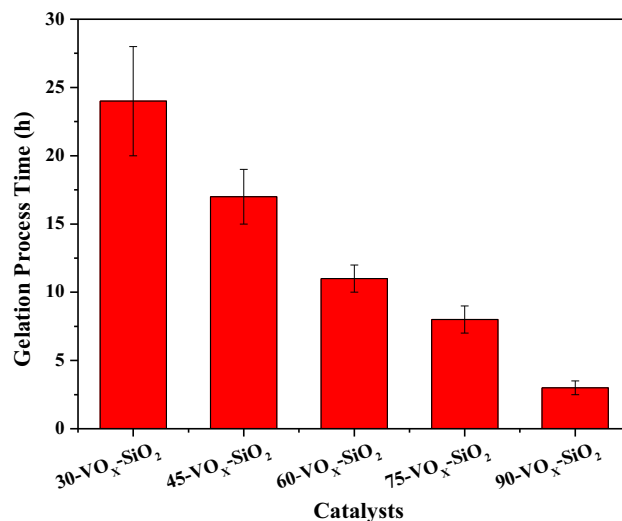


Fig. 1. The correlation between gelation time and temperature for  $\text{VO}_x\text{-SiO}_2$  catalysts calcined at 580 °C.

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