

Competitive reaction pathways in oxidative dehydrogenation of propane over monolayer V_2O_5/TiO_2 catalysts: Experiment and theoretical insights

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Abstract

Oxidative dehydrogenation of propane to propylene over a monolayer vanadia-titania catalyst was studied *in situ* using Fourier transform infrared spectroscopy (FTIRS). It was found that two types of active species capable of activating C–H bonds exist on the catalyst surface: vanadyl oxygen species (V = O) and hydroxyl groups (V–OH). The adsorption of propane onto vanadyl oxygen activates a C–H bond, subsequently initiating the transfer of a proton from the methylene group to another vanadyl oxygen, which leads to the formation of a new hydroxyl group and an isopropyl group. Alternatively, propane can adsorb onto a surface hydroxyl group to form a hydrogen-bonded complex. This surface complex is unstable and can decompose via the cleavage of a C–H bond in a methyl group, transferring the proton to the nearest vanadyl oxygen to form a new hydroxyl group and hydrogen-bonded n-propyl group. These findings indicate that the dehydrogenation of propane over the monolayer V_2O_5/TiO_2 catalyst can proceed via at least two distinct reaction pathways, initiated either by the adsorption of propane onto vanadyl oxygen species or onto the surface hydroxyl groups. The energy profiles for these pathways were calculated using the density functional theory (DFT). The DFT calculations demonstrated that the pathway initiated by the formation of a hydrogen-bonded complex between surface hydroxyl groups and propane is more thermodynamically favorable than the pathway starting with the adsorption of propane onto vanadyl oxygen species. In both pathways, two C–H bonds are cleaved and two protons are transferred to the vanadyl oxygen species to form new hydroxyl groups and propylene.

Introduction

Propylene is a vital chemical feedstock utilized in the production of many valuable chemicals, including polypropylene, acrylonitrile, propylene oxide, cumene, and acrylic acid [1, 2]. Currently, the bulk of propylene is generated as a by-product in steam cracking and fluid catalytic cracking processes. However, surging market demand has driven the development of alternative, on-purpose production technologies. Among these, the direct propane dehydrogenation (PDH) has attracted significant attention, fueled by the booming production of propane-rich shale gas [1–5]. Although non-oxidative PDH is already commercialized—relying primarily on platinum- or chromium oxide-based catalysts [4]—its widespread expansion is hindered by the prohibitive cost of platinum and the severe environmental hazards of chromium. Alternatively, the oxidative dehydrogenation of propane (ODHP) over non-toxic, transition metal oxide catalysts offers a promising solution. From a thermodynamic perspective, ODHP is highly advantageous: being exothermic, it achieves elevated propane conversion at lower temperatures. Furthermore, the continuous co-feeding of oxygen suppresses coke deposition, thereby ensuring long-term catalytic stability.

Among the various catalytic systems evaluated for ODHP, vanadium oxide-based catalysts remain the most commercially promising due to their high performance, cost-effectiveness, and environmental friendliness [1, 6–8]. This growing demand for on-purpose propylene production technologies has initiated a vast number of studies dedicated to dehydrogenation of propane over vanadia-based catalysts. However, most research has focused either on developing novel catalysts or on optimizing

existing ones to achieve industrially viable propylene yields [6], whereas relatively little attention has been paid to the reaction mechanism and the precise nature of the active sites. Previous studies have shown that the ODHP rate is proportional to propane pressure and generally independent of oxygen pressure [9, 10]. Propylene is the most abundant primary product; CO and CO₂ form via the secondary oxidation of propylene, while CO₂ is also generated through the direct combustion of propane. Kinetic measurements [1, 11] indicate that the dehydrogenation proceeds via a redox mechanism that is well-described by the Mars-van Krevelen model. The active sites are attributed to highly dispersed vanadia species on the support surface. Generally, the highest efficiency in catalytic reactions is demonstrated by the so-called monolayer catalysts, in which the entire surface of the support is covered with polymeric (VO_x)_n structures, free of low-active vanadium oxide nanoparticles [12, 13]. According to DFT simulations of the propane dehydrogenation [14], monomeric vanadia species (VO_x) are less active than vanadia dimers and oligomers. It is widely believed that the active sites contain V⁵⁺ cations, and the main debate centers on which oxygen species—vanadyl oxygen (V = O) or bridging oxygen (V–O–V) are involved in the activation of C – H bonds [14–17]. At the same time, hydroxyl groups are formed on the catalyst surface as a result of the propane dehydrogenation [7, 14]. We suggest that these OH groups can act as Brønsted acid sites (BAS) and may participate in C – H bond activation of as well [18, 19].

To elucidate the role of the vanadyl oxygen species and Brønsted acid sites in the dehydrogenation of propane over the monolayer V₂O₅/TiO₂ catalysts, an *in situ* FTIR spectroscopy study was performed. Additionally, a periodic model of the monolayer catalyst was developed incorporating multiple active sites, including vanadyl oxygen species and the surface hydroxyl groups. Energy profiles were calculated for two reaction pathways of the propane dehydrogenation, focusing on C – H bond activation occurring at either the vanadyl or hydroxyl-groups.

Experimental

Catalyst preparation

The monolayer V₂O₅/TiO₂ catalyst was prepared by incipient wetness impregnation using an aqueous solution of vanadyl oxalate, as describe in detail elsewhere [7]. Commercial Alfa Aesar TiO₂ (nanometer-scale anatase with a specific surface area of 350 m²/g) was used as the support. The catalyst was calcined in air at 400°C for 4 h, which reduced the specific surface area to 115 m²/g. Elemental analysis indicates that the catalyst contained 12.5 wt% V₂O₅, that corresponds to the surface vanadia coverage of approximately 0.9 monolayer. Raman spectroscopy confirmed that the catalyst contained exclusively polymeric surface vanadia species [7, 13]. No impurities were detected by X-ray photoelectron spectroscopy (XPS) on the catalyst surface.

In situ FTIRS experiments

In situ FTIRS studies were performed using an Agilent Cary 660 FTIR spectrometer equipped with a custom-made quartz cell-reactor [7]. The catalyst powder was pressed into a thin, self-supporting pellet (1 cm × 3 cm in size, 15 mg/cm²) and placed inside the cell-reactor. The cell-reactor was heated from room temperature to 350°C using an electric furnace. The catalyst temperature was measured via a K-type thermocouple. To detect surface reaction intermediates, *in situ* FTIR spectra were recorded in transmission mode at atmospheric pressure. The reactant feed contained 6 vol.% C₃H₈ and 6 vol.% O₂ in an Ar balance. The total flow rate was 120 sccm. The spectra were acquired at 150 and 300°C in the 1000–4000 cm⁻¹ range with a resolution of 4 cm⁻¹. The acquisition time of the spectra was approximately 40 s. Before the experiments, the catalyst was pretreated in flowing air at 350°C for 1 h. The catalyst was then cooled stepwise to record reference spectra at 300 and 150°C. To isolate the reaction intermediates, these reference spectra were subtracted from the raw FTIR spectra collected at the corresponding temperatures under the reaction mixture. All the spectra were recorded after a 10-minute stabilization period following gas introduction and temperature equilibration.

DFT calculations

Spin-polarized periodic DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [20]. The core–electron interactions were described by the projector-augmented wave (PAW) method [21, 22]. The electronic wave functions were expanded in a plane-waves basis set with a kinetic energy cutoff of 400 eV. Exchange-correlation energies were treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional [23]. The monolayer V₂O₅/TiO₂ catalyst was represented by a periodic slab model consisting of a 2×5 supercell of the anatase TiO₂ (001) surface topped with one epitaxial layer of V₂O₅, following the model developed by Alexopoulos and co-workers [17, 24]. The titania support comprised four atomic layers, and a 15 Å vacuum gap was introduced normal to the surface to prevent spurious interaction between periodic images [24]. Brillouin zone integration was performed using a 2×2×1 Monkhorst-Pack *k*-point mesh for all slab calculations [25]. During structural optimizations, the atoms in the bottom two layers of the TiO₂ support were fixed at their bulk positions to simulate the semi-infinite crystal background, whereas the top two layers, the vanadia overlayer, and the adsorbates were fully relaxed. To elucidate the role of Brønsted acid sites in the dehydrogenation of propane, half of the vanadyl groups (V = O) were replaced by hydroxyl groups (V–OH). Consequently, the co-existence of two distinct active species—vanadyl groups and Brønsted acid sites—was established within the model catalyst.

Results and discussion

Figure 1 shows a typical FTIR spectrum of the fresh monolayer V₂O₅/TiO₂ catalyst recorded under air flow. The spectrum exhibits two sharp bands at 3656 and 1609 cm⁻¹, corresponding to the stretching $\nu(\text{OH})$ and bending $\delta(\text{H}_2\text{O})$ vibration modes of the surface hydroxyl groups (V–OH) and adsorbed water molecules, respectively [26, 27]. Additionally, a weak band is observed near 2040 cm⁻¹, which is

attributed to the first overtone of the stretching $\nu(\text{V}=\text{O})$ vibration mode of the surface vanadyl species [7, 26, 27]. The band is broad and features additional maxima at 2028 and 2019 cm^{-1} , which is explained by the non-uniform coverage of the titania surface with vanadium oxide species [27]. The fundamental $\nu(\text{V}=\text{O})$ stretching band at approximately 1035 cm^{-1} overlaps with strong absorption bands arising from the TiO_2 lattice vibrations.

These findings demonstrate that both vanadyl and hydroxyl groups are present even in the fresh catalyst. Unfortunately, the absolute or relative concentrations of these surface species cannot be quantified, as this requires either knowing the molar absorption coefficient or performing a spectrophotometric calibration against a known quantity of both species. Nevertheless, it can be speculated that the molar absorption coefficient for the first overtone of the stretching $\nu(\text{V}=\text{O})$ vibration mode is lower than that of the fundamental $\nu(\text{OH})$ stretching band. Moreover, according to the previous X-ray photoelectron spectroscopy study [7], the fresh monolayer $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst treated in O_2 contains only 8–10% of vanadium in the V^{4+} state and 90–92% in the V^{5+} state. This indicates that the concentration of hydroxyl groups is at least an order of magnitude lower than that of vanadyl groups in the fresh $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, since hydroxyl groups are typically bonded to the V^{4+} cations. Indeed, generally, the hydration of transition metal oxide surfaces induces a redistribution of electron density and the partial reduction of cations. In the case of vanadia, the formation of hydroxyl groups is accompanied by the reduction of V^{5+} to V^{4+} [7].

To elucidate the mechanism of C–H bond activation, *in situ* FTIR spectra of the catalyst were collected under a propane/oxygen mixture at 150 and 300°C. The difference spectroscopy technique was applied to monitor the dynamic structural changes occurring under reaction conditions. The difference spectra were obtained by subtracting the reference spectra (acquired at the same temperature under air flow) from the *in situ* spectra. It is well known that difference spectra can feature both “negative” and “positive” absorption bands: the “negative” bands correspond to functional groups and structures removed from the catalyst surface, whereas the “positive” bands correspond to the appearance of new surface species. The resulting difference spectra of the catalyst are shown in Fig. 2.

The FTIR spectrum recorded at 150°C exhibits a number of bands assigned to gas-phase propane. The most intense bands are observed in the C–H stretching region (3300–2800 cm^{-1}). Specifically, the band at 2965 cm^{-1} , with pronounced shoulders at 2980 and 2957 cm^{-1} , along with overlapping bands maximizing at 2902, 2888, and 2872 cm^{-1} , correspond to the symmetric and asymmetric CH_2/CH_3 stretching modes of gas-phase propane [7, 28]. In addition, the spectrum contains several bands in the C–H in-plane bending vibration region (1500–1300 cm^{-1}). These include weak triplets with maxima at 1454, 1470, and 1485 cm^{-1} as well as at 1360, 1375, and 1394 cm^{-1} , matching the P, Q, and R branches of the CH_3 asymmetric and symmetric bending vibrations in gas-phase propane, respectively. In the O–H stretching region (3200–3650 cm^{-1}), a negative band at 3658 cm^{-1} and a broad positive band near 3609 cm^{-1} are resolved. The negative band points to the interaction of surface V–OH groups with propane

molecules, leading to the formation of a hydrogen-bonded complex between surface hydroxyl groups and the alkane [18]. Indeed, the band at 3609 cm^{-1} is assigned to the hydroxyl groups involved in hydrogen bonding. These findings indicate that propane adsorption and activation proceed on the surface V–OH groups. Concurrently, the spectrum features a negative band near 2043 cm^{-1} , indicating the interaction of propane with the vanadyl oxygen species.

The FTIR spectrum recorded at 300°C also exhibits several bands assigned to gas-phase propane; however, their intensity is lower due to the partial conversion of propane to propylene. Furthermore, heating leads to the appearance of two strong bands at 1528 and 1440 cm^{-1} , which can be assigned to surface acetate species. Indeed, bridging bidentate acetates on the surface of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts are characterized by similar bands at 1520 – 1528 and 1444 cm^{-1} , corresponding to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ vibrational modes, respectively [29]. It should be noted that these acetate species do not participate in the dehydrogenation of propane. Moreover, they block the catalyst surface, thereby suppressing propylene formation; while their decomposition yields CO_2 . The intensity of the band at 3609 cm^{-1} decreases, confirming the low thermal stability of the hydrogen-bonded complex. In contrast, the amplitude of negative band at 2040 cm^{-1} increases, indicating the direct involvement of vanadyl oxygen species in the propane dehydrogenation. This process is accompanied by the appearance of a band at 3670 cm^{-1} , which corresponds to the surface hydroxyl groups.

In summary, the FTIRS data demonstrate that the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst surface features two distinct active species capable activating C–H bonds in propane: vanadyl oxygen species and hydroxyl groups. The first pathway of the dehydrogenation involves adsorption of propane on vanadyl oxygen, which activates a C–H bond and triggers a subsequent proton transfer from the CH_2 group to adjacent vanadyl oxygen, yielding a newly formed hydroxyl group and an isopropyl intermediate; this mechanism has been discussed in detail elsewhere [7]. Alternatively, propane can interact with a surface hydroxyl group to form a transient hydrogen-bonded complex. This unstable intermediate undergoes decomposition via C–H bond cleavage within a methyl group, followed by proton transfer to the nearest vanadyl oxygen to generate a new hydroxyl group and an n-propyl species. To the best of our knowledge, this alternative pathway has not been previously reported for the dehydrogenation of propane to propylene over $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts.

To gain insight into the reaction mechanism, DFT calculations were performed for two propane dehydrogenation pathways involving C–H bond activation on either the vanadyl oxygen species or the surface hydroxyl groups. The monolayer $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst was represented by a periodic slab model consisting of the anatase $\text{TiO}_2(001)$ surface topped with a single epitaxial layer of vanadium oxide [17, 24]. A distinctive feature of our model is the simultaneous presence of both vanadyl oxygen species and surface hydroxyl groups on the catalyst surface, achieved by replacing half of the vanadyl groups of V_2O_5 with hydroxyl groups.

The calculated energy profiles for the propane dehydrogenation pathways over the monolayer V_2O_5/TiO_2 catalyst are shown in Fig. 3. The first pathway proceeds exclusively via the vanadyl oxygen species. This mechanism initiates with the adsorption of propane onto the surface oxygen. Notably, experimental data indicate that C–H bond cleavage at the methylene group is both thermodynamically and kinetically more favorable than at the methyl group (see ref. [30] and references therein). Several theoretical studies have also shown that the activation barrier for breaking the C–H bond of the methyl group is higher than that of the methylene group [16, 30]. Although the vanadia surface features two distinct oxygen species—terminal vanadyl ($V=O$) and bridging ($V-O-V$) oxygens—Fu and co-workers [16] demonstrated that both activate the C–H bond of propane with similar activation barriers. This allowed us to limit our consideration to one most probable route of propane dehydrogenation (Fig. 3). In this pathway, one of the vanadyl groups attacks the β -C atom of propane, converting it into a $V-OCH_2(CH_3)_2$ species. Subsequently, the C–H bond breaks, and the proton is transferred to another vanadyl group, transforming it into a V–OH group. This process is exothermic; the formation of the new hydroxyl group and the isopropyl intermediate leads to an energy drop of 36 kcal/mol. The subsequent step involves C–H bond cleavage at the methyl group, followed by another proton transfer to an adjacent vanadyl oxygen, yielding a second hydroxyl group. This process is also exothermic; the resulting formation of propylene and a hydrated catalyst surface lowers the system energy by 98 kcal/mol (Fig. 3). Following the desorption of propylene, the catalytic cycle is closed by the interaction of two adjacent V–OH groups. This leads to the formation of a water molecule and an oxygen vacancy, with subsequent adsorption of gas-phase oxygen that fills the vacancy and restores the catalyst.

The second pathway initiated with the adsorption of propane onto the surface hydroxyl group (Fig. 3). Using DFT calculations, we identified a stable, hydrogen-bonded complex where the propane molecule interacts with the surface hydroxyl group via a hydrogen atom of its methyl group. This localized adsorption leads to a significant energy reduction of 74 kcal/mol, which exceeds the stabilization energy observed for propane adsorption onto the vanadyl group. Subsequently, a hydrogen atom is abstracted from the methyl group and transferred to the nearest vanadyl oxygen, yielding a new hydroxyl group. A second hydrogen atom is then abstracted from the methylene group and transferred to an adjacent vanadyl oxygen atom. Consequently, much like the first mechanism, this step produces propylene and two surface hydroxyl groups. The catalytic cycle is also completed by the elimination of water and the subsequent adsorption of oxygen from the gas phase. Notably, this second pathway proves to be thermodynamically more favorable.

It is worth noting that propane dehydrogenation via adsorption onto surface hydroxyl groups is a well-established concept. Previously, Gounder and Iglesia [31] demonstrated that Brønsted acid sites within zeolite channels catalyze alkane dehydrogenation via monomolecular pathways. This process involves carbonium-ion-like $(C-H-H)^+$ transition states during the kinetically-relevant C–H bond scission steps. A similar mechanism of C–H bond activation in propane over Brønsted acid sites has also been proposed for gallium promoted H-ZSM-5 catalysts [19, 32]. In the latter case, the reaction is initiated by the protonation of the methylene C – H bond of propane, which subsequently dissociates to form an

isopropyl cation and H₂. The isopropyl intermediate then transfers a methyl proton to a framework oxygen, yielding propylene and generating a new hydrogen group.

Conclusions

In situ FTIRS study confirms the existence of two types of active species on the surface of the monolayer V₂O₅/TiO₂ catalyst: vanadyl oxygen species and hydroxyl groups. These species can activate C–H bonds in propane, enabling the dehydrogenation of propane to propylene. DFT calculations predict that the dehydrogenation pathway initiating from the formation of a hydrogen-bonded complex between a surface hydroxyl group and propane is thermodynamically more favorable than the pathway starting with the adsorption of propane on the vanadyl oxygen species. In both reaction routes, two C–H bonds are broken, and two protons are transferred to the vanadyl oxygen species to form new hydroxyl groups and propylene. Following the desorption of propylene, the catalytic cycle is completed by the interaction of two adjacent V–OH groups. This leads to the formation of a water molecule and an oxygen vacancy, followed by the subsequent adsorption of gas-phase oxygen, which fills the vacancy and restores the catalyst.

Declarations

Conflict of interest

The authors declare no competing interests.

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Author Contribution

Conceptualization: VVK, supervision: VVK and DAP, methodology: VVK, investigation, visualization and validation interpretation of data: YAC and DAP, writing-original draft: VVK, writing review and final editing: VVK and DAP.

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Data Availability

The authors confirm that the data supporting the findings of this study are available within the article.

Footnotes

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Figures

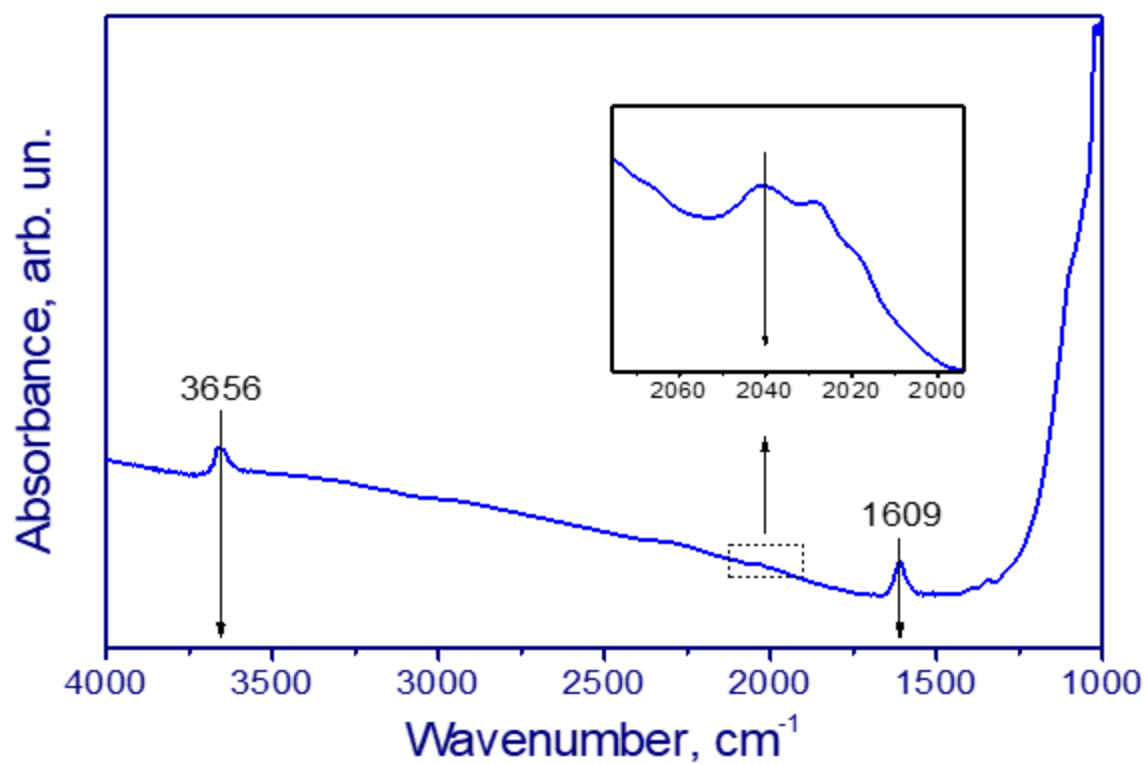


Figure 1

In situ FTIR spectrum of monolayer V₂O₅/TiO₂ catalyst under air flow at 150 °C.

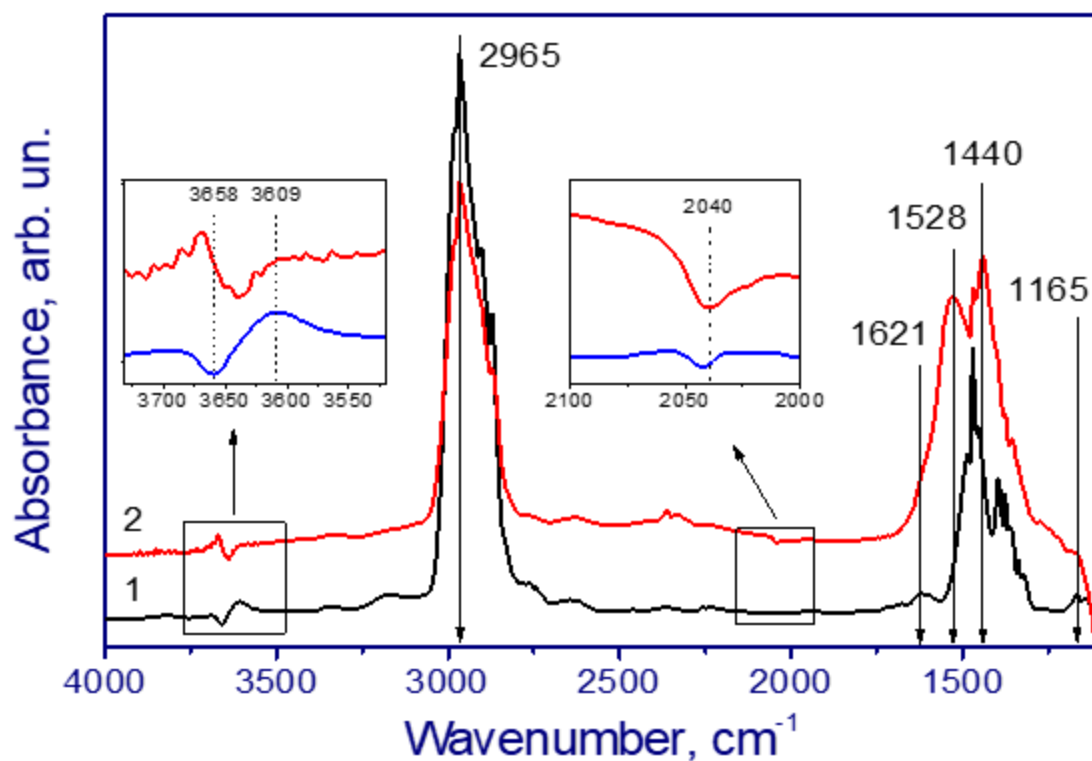


Figure 2

Difference FTIR spectra of the monolayer $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst recorded during oxidative dehydrogenation of propane at 150 °C (1) and 300 °C (2). Feed gas: 6 vol.% C_3H_8 , 6 vol.% O_2 , balanced with Ar.

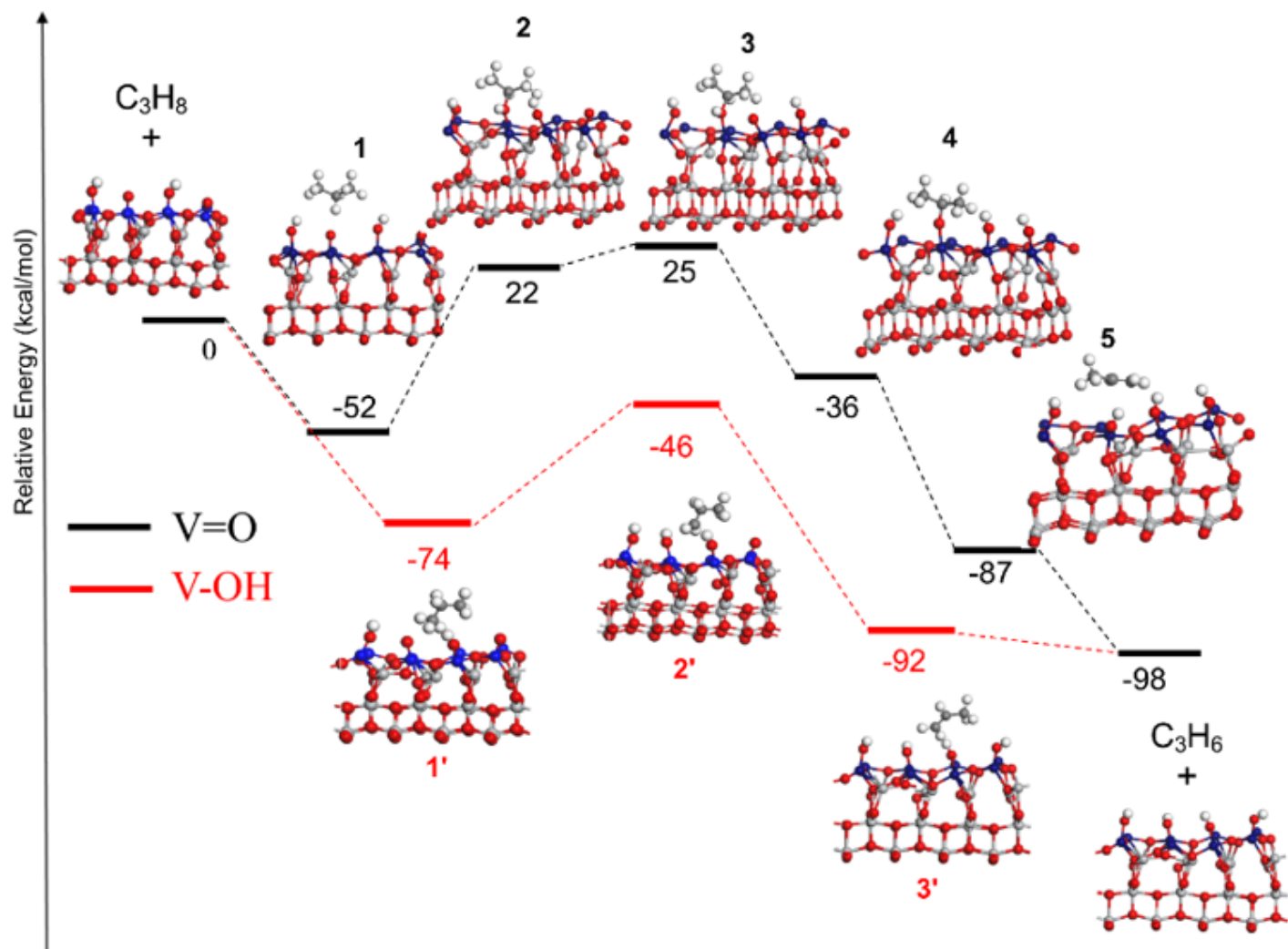


Figure 3

The calculated energy profiles for two routes of dehydrogenation of propane to propylene over monolayer $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst.