Catal Lett (2009) 128:256–262
DOI 10.1007/s10562-008-9701-4

Vanadium Oxide Based Nanostructured Materials: Novel Oxidative Dehydrogenation Catalysts

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Received: 10 June 2008 / Accepted: 23 September 2008 / Published online: 15 October 2008

Abstract Novel vanadium oxide based catalyst derived from the open-framework solid, $[Co_3V_{18}O_{42}(H_2O)_{12}(XO_4)]\cdot 24\ H_2O$ ($X = V, S$) (**1**) catalyses oxidative dehydrogenation of propane to propylene. Catalyst activity was evaluated in the temperature range 250–400 °C with varying gas hourly space velocity (GHSV). At 350 °C and GHSV of 9786 h^{-1} and at 1.3% propane conversion the selectivity to propylene was 36.8%. The major products obtained were propylene and CO_x (CO_2 and CO). The ratio of the propylene to CO_x depended directly on the catalytic sites present. Thus, as the amount of the catalyst was decreased, the conversion decreased with an increase in the propylene selectivity and a decrease in the selectivity to carbon oxides—CO_x. The catalyst has been characterized by temperature programmed reduction and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

Keywords Oxidative · Dehydrogenation · Catalysis · Propylene · Framework solid · Polyoxometalates · DRIFTS

1 Introduction

Oxidative dehydrogenation (ODH) for olefin production is receiving increasing attention as an alternative route to dehydrogenation and steam cracking processes [1–6]. Being an exothermic process, ODH does not require high temperature and is much simpler compared to currently employed commercial technologies (or processes). Most ODH catalysts studied so far are composed of supported vanadium–oxides [7, 8], vanadium–antimony [9–13], vanadium–molybdenum [14–16] and vanadium–phosphorous [17, 18]. Most selective ODH catalysts reported until now consist of {V/Mg mixed oxides}, $\{Ni(Co)MoO_4\}$, {V–Nb–O}, {V–Zr–Si–O}, $Ni\{MoO_4\}$, {K–Mo–Si–Ti–O} and V-Silicate based systems [19–26].Although there are some controversies about the catalytic sites involved, in most cases the active sites are attributed to *ortho*-vanadate, *pyro*-vanadate and isolated $\{VO_4\}$ tetrahedra. Further studies are needed to have a better understanding of the catalysts' active and selective sites in these systems and to improve their performances.

Polyoxometalates (POMs) or transition metal oxide clusters provide a class of materials that are attractive precursors to a new generation of promising ODH catalysts. POMs exhibit rich structural and electronic properties and offer a unique opportunity for introducing systematic variation in the microstructure (such as coordination geometry and oxidation states of metal centers/active sites) of the catalysts. This control is significant in the context of developing strategies for fine-tuning catalyst properties at the molecular level. However, with the exception of a few fragmentary reports describing the ODH catalytic activities of Keggin-type polyoxometalates (which have robust and thermally stable structures and readily prepared) [27, 38–41], the POMs have not been studied, systematically, as ODH catalysts.

In view of the limited information available on the active sites and reaction mechanism involved in ODH catalysis, design and development of efficient ODH catalysts remains a challenge. In order to address these problems, a better understanding of the structure—activity relationship in the

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catalysts is needed requiring a new generation of catalyst materials with well-defined structures. Such a class of materials has recently been described in the form of synthesis and characterization of a series of novel vanadium oxide (or polyoxovanadate) based solids [28–32]. The structures of these materials are determined at atomic resolution by using X-ray crystallography and spectroscopic methods. In view of the crucial role of vanadium in improving the performance of ODH catalysts, such as VMgO [33, 34] and V_2O_5 on different supports [35–37] (e.g. silica, alumina, boria, titania etc), these new class of vanadium oxide based materials are especially relevant for ODH catalysis. Their structures can be modified at the molecular level, offering the possibility of fine-tuning of the microstructure of catalysts. Thus, they offer an opportunity to gain a better understanding of the active and selective sites involved in the catalysis as well as the structure–property relationship of the catalyst system.

This work demonstrates the ODH catalysis of propane by novel ODH catalysts derived from the new class of vanadium oxide based open-framework materials. Here we report a preliminary study of the oxidative dehydrogenation of propane to propylene by the catalysts derived from the vanadium oxide based framework solid $[Co_3V_{18}O_{42}(H_2O)_{12}(XO_4)].24\ H_2O$ (X = V, S) (**1**).

2 Experimental Section

2.1 Catalyst Preparation

The open-framework material **1** used for catalysis were synthesized by employing a one-pot synthetic method described elsewhere [40]. Catalysts used in this work were tested as synthesized. Prior to testing 500 mg of sample **1** was mixed with 500 mg of SiC and crushed into a homogeneous mixture.

2.2 Catalytic Experiments

Catalytic activity measurement at atmospheric pressure for ODH of propane were performed in the temperature range 250–400 °C in a fixed bed tubular downflow quartz laboratory reactor, shown in the experimental set-up in Fig. 1. The catalyst samples used in the experiment were varied from 136 to 1000 mg, diluted with 500 mg SiC (Electro Abrasive) in order to increase the bed size and to avoid heat transfer effects. The feed mixture consisted of 3% C_3H_8/Ar, and 20% O_2/Ar creating a 1:1 C_3H_8:O_2 ratio.

Prior to testing, the catalyst was treated in a flow of oxygen for 1 h at 400 °C. The reactor used in this work was made of a long quartz tube tapered at the bottom. The tapered portion was filled with quartz pieces for fast removal of the reaction gases to minimize gas-phase reactions. Catalysts were placed in the reactor with a plug of quartz wool directly above the reaction zone.

A thermocouple was placed both outside the catalyst bed and at the center of the catalyst bed at all time during the experiment to monitor the sample temperature. A Hewlett–Packard Series II 5890 Gas-Chromatograph equipped with a thermal conductivity detector was used to separate and analyze the reaction products. Molecular sieve and RT-QPLOT columns were used to analyze O_2, CO, CO_2 and hydrocarbons, respectively. The products were allowed to flow directly through a heat-traced line to the GC sampling

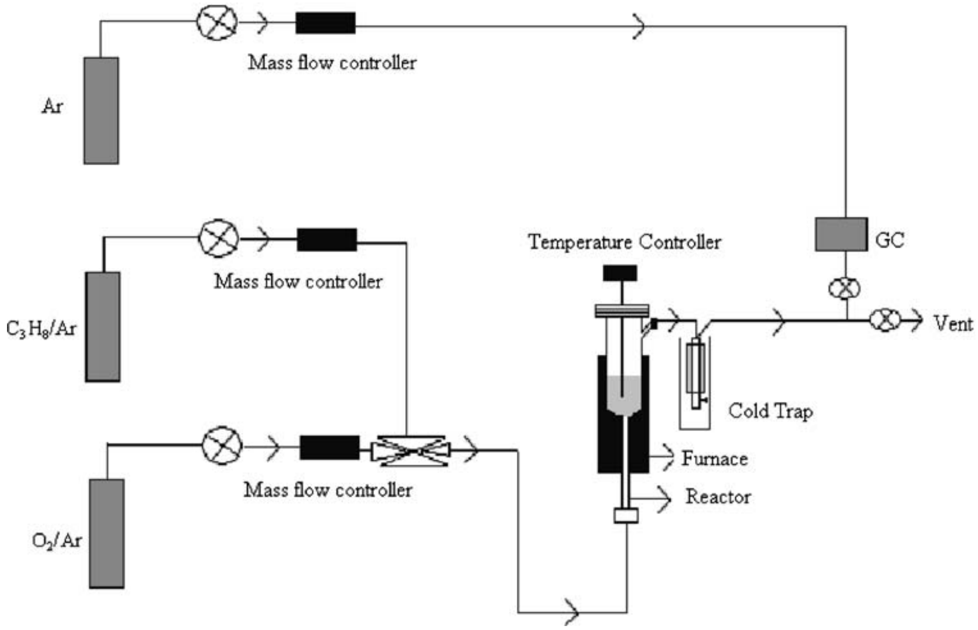

Fig. 1 Experimental set-up

valve. A cold trap was used to retain the water produced during the experiment and to avoid condensation in the cold parts of the apparatus.

Catalyst performance was measured in terms of Conversion (%) and Selectivity (%), which are defined below:

$$\text{Conversion}(\%) = \frac{\text{moles of carbon in products}}{\text{Total moles of carbon input}} \times 100$$

$$\text{Selectivity of product X}(\%) = \frac{\text{moles of carbon in product X}}{\text{Total moles of carbon input}} \times 100$$

Carbon balances were greater than 95%. A blank test performed in the presence of SiC without the catalyst showed negligible conversion of propane under the reaction conditions described above.

2.3 Catalyst Characterization

The gases used in the catalyst testing as well as catalyst characterization were obtained from Linde gas or AGA. Temperature programmed reduction (TPR) was performed on an Altamira AM-1 unit equipped with a thermal conductivity detector (TCD). All the outlet gases were analyzed by a Dycor Dymaxion quadrapole mass spectrometer. Initially, about 50 mg of the sample was loaded into a 1/8-in. quartz U-tube and installed into the apparatus with the help of Swagelok fittings. Before each TPR runs, the catalyst sample was heated in O_2/He (5%) at 400 °C for 15 min at a rate of 25 mL/min and then cooled to room temperature. Thereafter, the samples were flushed in Ar (99.9%) followed by feeding of 25 mL/min H_2/Ar (3%) to 500 °C at a rate of 5 °C/min.

Surface area was determined using the method of Brunauer, Emmett and Teller (BET). Nitrogen adsorption–desorption at liquid nitrogen temperatue (77 K) was measured on a Micromeritics ASAP 2010 instrument. Prior to the measurement, the sample was degassed at 150 °C overnight in order to ensure a clean and dry surface.

Diffuse Reflectance Infrared Spectroscopy (DRIFTS) was employed to do in situ investigation of structural changes during the catalysis experiments. For this purpose, a FTLA2000-104 spectrometer from ABB equipped with a Harrick Scientific DRP-BO5 praying mantis housing a high temperature diffuse reflectance cell was used. Infrared radiation was produced with the help of a SiC source. The reflected radiation was collected by a praying mantis optical attachment and re-directed to a DTGS detector. The gas mixture of 13.3% C_3H_8/Ar and 6.7% O_2/Ar was blended on a manifold system upstream of the cell. DRIFTS was performed with a freshly prepared neat catalyst sample. About 100 mg of this mixture was loaded on a cup sitting on top of the heating cartridge of the cell. The dome of the cell maintained a controlled environment around the sample during the experiment. Prior to the experiment, the sample was flushed in N_2. The spectrum was collected at room temperature, after calcining to 400 °C in 20% O_2/Ar and at 350, 400 and 450 °C respectively, in 13.3% C_3H_8/Ar and 6.7% O_2/Ar. Spectra were averaged over 300 scans in 4,000–400 cm^{-1} range with a resolution of 2 cm^{-1}. The spectra were collected at each temperature after an equilibrium time of 20 min.

3 Results and Discussion

3.1 Catalyst Activity and Selectivity

As noted earlier, the catalytic performance tests were carried out in the temperature range 250–400 °C, using catalysts amounts of 136, 500 and 1,000 mg. The summary of the data showing catalysts' performance for the ODH of propane is given in Table 1.

Figure 2 shows the temperature dependence of the activity of the catalyst **1** at different GHSV's. In general, propane conversion increases with increasing temperature. At GHSV 1329 h^{-1}, as the temperature increases from 250

Table 1 Conversion and Selectivity of **1** for ODH of propane (GHSV = 1,329, 2,659 and 9,786 h^{-1}, C_3H_8:O_2 = 1:1)

Temperature (°C)	250	300	350	400
GHSV = 9,786 h^{-1}				
Conversion (%)				
C_3H_8	0.2	0.2	1.3	2.3
O_2	0.2	0.9	2.9	9.3
Selectivity (%)				
C_3H_6	100.0	100.0	36.8	25.9
CO	0.0	0.0	25.9	27.2
CO_2	0.0	0.0	37.3	46.9
GHSV = 2,659 h^{-1}				
Conversion (%)				
C_3H_8	0.1	0.2	1.0	3.9
O_2	0.8	2.9	6.9	29.4
Selectivity (%)				
C_3H_6	100.0	100.0	31.5	17.9
CO	0.0	0.0	41.0	52.9
CO_2	0.0	0.0	27.5	29.5
GHSV = 1,329 h^{-1}				
Conversion (%)				
C_3H_8	1.1	4.2	12.3	24.0
O_2	4.1	15.1	48.8	85.3
Selectivity (%)				
C_3H_6	42.5	25.3	12.5	5.6
CO	57.4	54.5	63.2	72.1

to 400 °C the propane conversion increases from 1.1% to 24.0%. A similar trend is observed at all other GHSV's described in this work. However, the overall propane conversion decreases with increasing GHSV, as shown in Fig. 1 for GHSV 2,659 and 9,786 h^{-1}.

Figure 3 shows the effect of temperature on the selectivity of the catalyst at the three GHSV's (1,329, 2,659 and 9,786 h^{-1}). Clearly, increasing temperature results in a decrease in the propylene selectivity, irrespective of the GHSV. At 1,329 h^{-1}, the selectivity to propylene at 250 °C was 42.5% (propane conversion = 1.0%). The selectivity decreased to 5.6% at 400 °C. Similarly, at GHSV 2,659 and 9,786 h^{-1}, the selectivity decreased from 100.0% at 250 °C to 17.9% and 25.9%, respectively, at 400 °C.

The selectivity to carbon dioxide (shown in Fig. 4) increases rapidly as temperature is increased from 250 to 300 °C, at GHSV 1,329 h^{-1}. The change in selectivity is, however, not as dramatic between 300–400 °C. At 2,659 and 9,786 h^{-1}, no CO_2 was formed at 250 °C and 300 °C. The only products formed were propylene and CO. At GHSV of 2,659 h^{-1}, increasing the temperature from 300 °C to 350 °C led to a rapid increase in the production of CO_2. This increase in CO_2 level continued at 400 °C, albeit at a slow pace. At 9,786 h^{-1}, there was a considerable increase in the CO_2 selectivity from 300 to 400 °C.

At GHSV 1,329 h^{-1}, the CO selectivity increased considerably from 57.5% at 250 °C to 72.1% at 400 °C. No CO was produced at temperatures lower than 350 °C at GHSV's 2,659 and 9,786 h^{-1}. The selectivity to CO increased from 41.0% at 350 °C to 52.9% at 400 °C at 2659 h^{-1}. But at 9786 h^{-1} GHSV, no considerable change in the selectivity of CO was observed upon increasing the temperature from 350 to 400 °C.

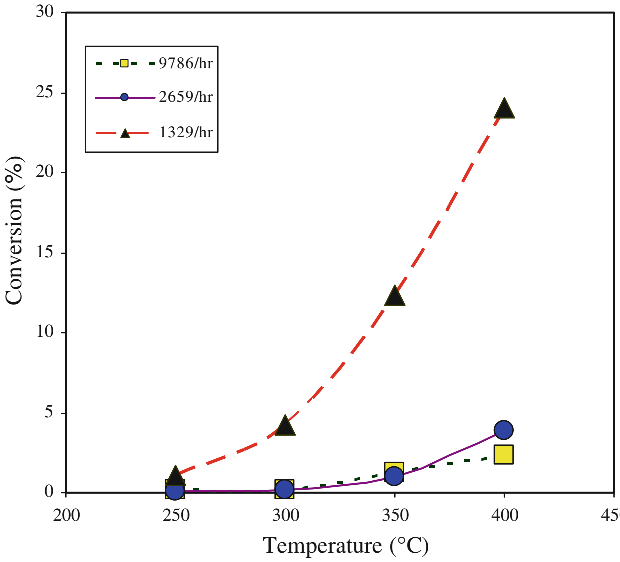

Fig. 2 Conversion versus temperature at different GHSVs by catalyst **1** (1,329, 2,659 and 9,786 h^{-1})

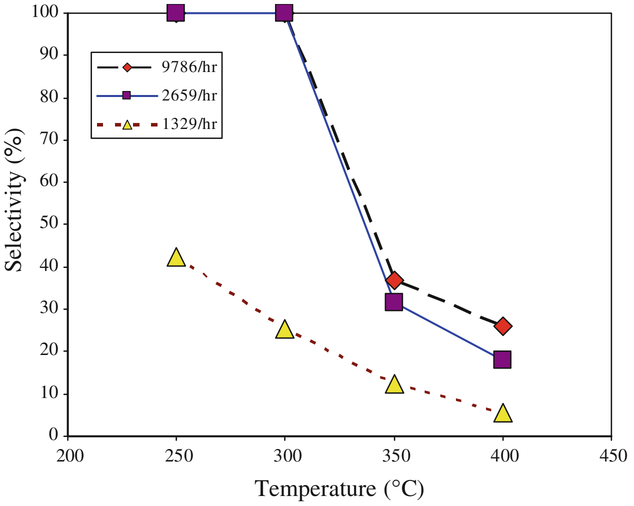

Fig. 3 Effect of temperature on the selectivity of propylene (C_3H_6) at different GHSVs by catalyst **1**

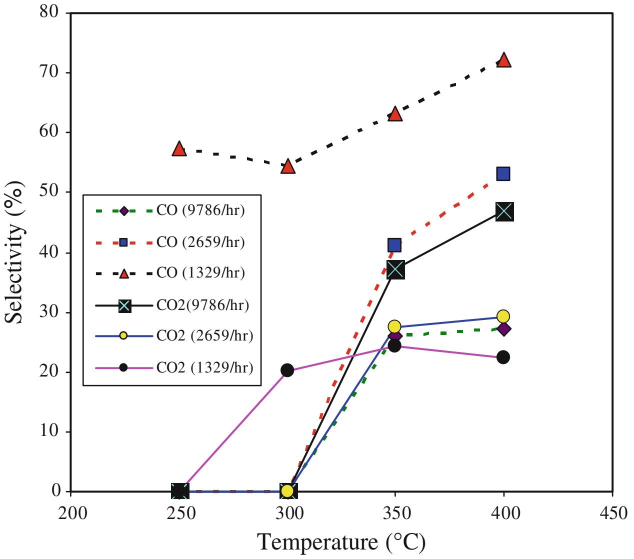

Fig. 4 Selectivity to carbon oxides as a function of Temperature and GHSVs by catalyst **1**

The results described above demonstrate the effect of space velocity on the catalyst activity and selectivity. It was observed that as the amount of the catalyst was decreased the propylene selectivity increased accompanied by an increased CO selectivity and a decreased CO_2 selectivity. Figure 5 shows the comparison between the selectivity to C_3H_6, CO and CO_2 at 350 °C at different gas hourly space velocity.

As the amount of the catalyst was increased (i.e. decreasing the GHSV), conversion of propane increased at the cost of selectivity. Lower space velocities lead to readsorption of intermediate products (such as propylene) resulting in the formation of deep oxidation products.

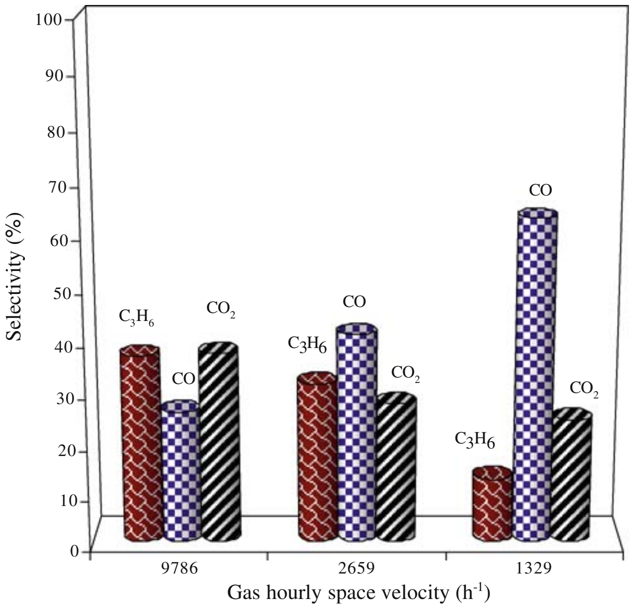

Fig. 5 Comparison between the selectivity's of C_3H_6, CO and CO_2 at 350 °C and three different space velocities by catalyst **1**

Hence, it was found that the catalyst selectivity depends directly on the space velocity.

From the above results it can be concluded that changing the amount of the catalyst led to change in the total number of catalytic sites. As the amount of the catalyst (and hence the active sites) is increased, the conversion increased due to the increase of the catalytic sites and vice versa. The major reaction products were C_3H_6, CO and CO_2. The decrease in propylene selectivity with a decrease in space velocity is accompanied by an increase in the CO selectivity and a decrease in the CO_2 selectivity. As the temperature increased the propylene selectivity decreased.

Keggin-type polyoxometalates have been studied to some extent as ODH catalyst due to their high thermal stability, robust structure and ease of preparation [38]. Al-Zahrani et al. reported that the Keggin compound, $K_3PW_{12}O_{40}$, showed ODH activity with 43% conversion of propane and 71% selectivity to olefins (propylene and ethylene) at 550 °C. They found that propylene selectivity decreases with temperature and/or the acid–base character of the catalyst [39]. Davis et al. studied catalytic ODH of propane by three heteropolyacids, namely, $H_3PMo_{12}O_{40}$ (PMo), $H_4PMo_{11}VO_{40}$ (PMoV) and Cu, V heteropolyacid (P/Mo/Cu/V/O) for ODH of propane. They observed that the activity of the catalyst containing Cu and V centers was greater than that of $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$ at 300 °C. Presence of copper ions helped to enhance the rate of oxidative dehydrogenation of propane [36]. Védrine et al. reported that the redox and the acidic properties of the heteropolyoxometalate species $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ could be fine tuned by introducing a redox metal center (M) such as Co (II), Fe (II), Ga (III), Ni (II), Zn (II) in a V:M ratio of 1:1. Fine-tuning the redox and acid properties of the catalysts resulted into enhanced selectivity for propylene (60–80%) at 5% and 10% conversion at 300–400 °C [41].

Magnesium vanadates, which have shown great catalytic activity in the recent years, have received considerable attention. There is, however, some controversy regarding the active phase of these catalysts [6, 7, 42, 43]. Kung and coworkers have done a systematic investigation of V/Mg/O catalysts. They have reported high propylene selectivity (62% selectivity, 8.4% conversion) at 500 °C. Supported vanadium oxide has also been studied considerably for oxidative dehydrogenation of propane. Interestingly, the reactivity of the catalyst increases due to the changes in the physico- chemical properties of the catalyst [35, 44, 45]. The selectivity of these supported catalysts is less than 40% at low conversion in the temperature range 350–450 °C (yield >10%).

Surface area measurements were performed for as prepared sample, after pretreatment at 400 °C and post catalysis samples of the catalyst. Both as prepared and post treated sample showed a very low surface area. However, the post catalytic sample exhibited a considerable increase in the surface area (~13.9 m^2/g).

Temperature Programmed Reduction (TPR) studies on a catalyst sample showed the presence of three peaks. The TPR data is shown in Fig. 6. This indicates that hydrogen consumption occurred in three stages resulting in the reduction of catalyst starting at a low temperature of ~282 °C. The first reduction occurs at ~282 °C followed by the second reduction at ~384 °C and is completed at ~422 °C. The presence of these multiple peaks is evident of the fact that there exist multiple redox sites on the catalyst surface. The peaks at 384 and 422 °C can be attributed to the reduction of Co^{+2} to metallic Co, which continues to 500 °C [46]. Since the catalyst was reduced at the above temperatures the reaction was carried out from 250 to 400 °C.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) provides an insight of the catalytic ODH reaction by following the course of catalyzed reaction and any structural changes in the catalyst.[1] The results of this study are summarized in Fig. 7. When the catalyst sample was flushed with N_2 at room temperature (Fig. 7a) a broad band appeared at 3507 cm^{-1} and a sharp band at

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[1] While as prepared catalyst material is highly crystalline with a well-defined XRD pattern and resolved crystal structure, the catalyst loses its crystallinity upon heating as evidenced by the broad peaks in the X-ray powder diffraction patterns of the pretreated (at 350 and 450 °C) catalyst as well as the catalyst recovered after the catalyst testing experiments. Thus, DRIFTS provides an insight of structural changes in the catalyst framework following pretreatment and ODH catalysis experiments.

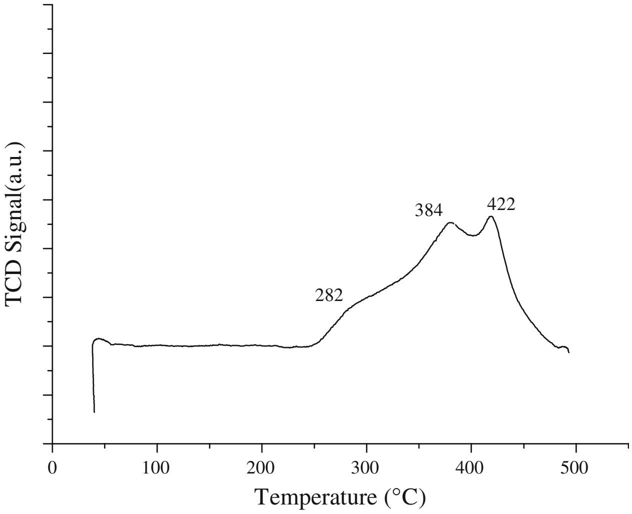
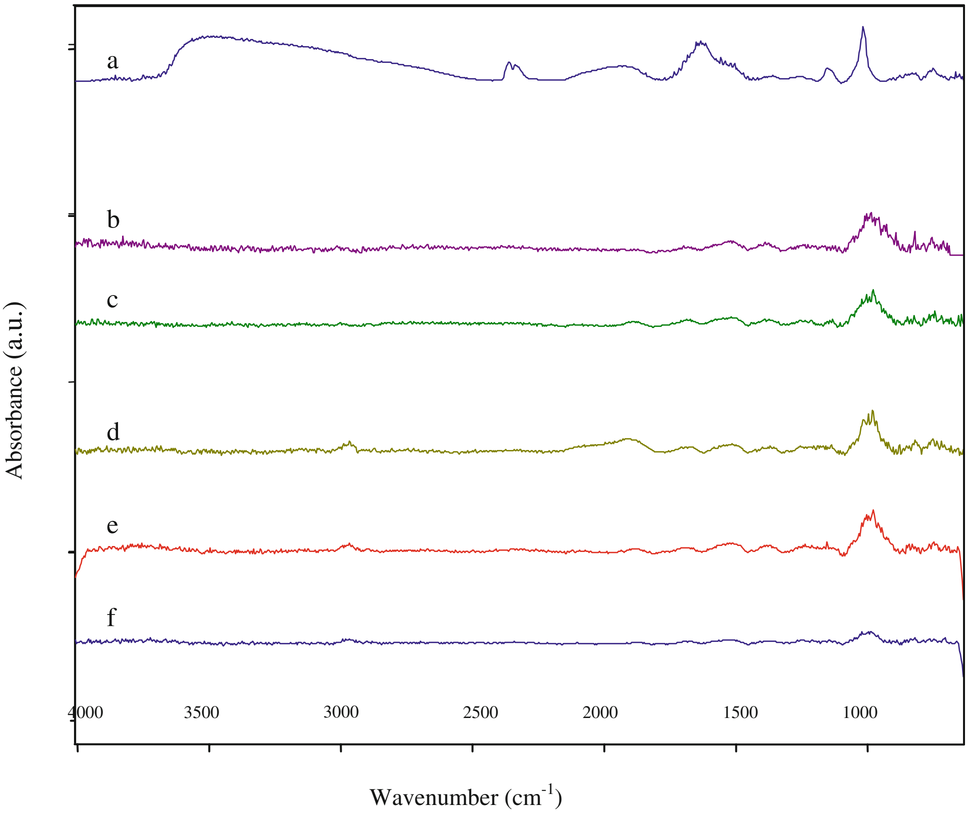


Fig. 6 H_2-TPR profile of catalyst **1**

1621 cm^{-1} that are attributable to the O–H stretching and bending vibrations, respectively, from the coordinated water present in the catalyst. Sharp bands at 1151 and 1015 cm^{-1} is due to V=O stretching. The doublet at 2,363 and 2,333 cm^{-1} was due to atmospheric CO_2. When the catalyst sample was heated to 400 °C in N_2, the bands at 3,507 and 1621 cm^{-1} disappeared (Fig. 7b). This is clearly due to the loss of coordinated water molecules. Furthermore, broadening of the V=O stretching bands are indicative of the changes in the framework structure of the catalyst [see footnote 1]. Similar observation was made when the catalyst sample was exposed to 20% O_2/Ar at 400 °C for 1 h (Fig. 7c).

The temperature was then lowered to 350 °C (Fig. 7d) and a mixture of 13.3% C_3H_8/Ar and 6.7% O_2/Ar was introduced in the DRIFTS cell (simulating the catalysed ODH reaction) and the mixture was allowed to reach the equilibrium state for 20 min followed by spectral data collection and observation. A sharp band appeared at 2,964 cm^{-1}, which is assigned to C–H stretching vibration from the reactant propane molecule, followed by satellite bands at 2,903 and 2,883 cm^{-1} due to the $-CH_2$ stretching vibrations. No further change in the catalyst structure was observed (as seen from the Fig. 7b–d). In order to find out if the propane was adsorbed on the catalyst surface, the DRIFTS cell compartment was flushed with N_2 for 5 min. This caused complete disappearance of the bands due to propane. But they reappeared, again, when the gas mixture (13.3% C_3H_8/Ar + 6.7% O_2/Ar) was reintroduced in the cell. These observations indicate that the gases were only physisorbed on the catalyst surface rather than being chemisorbed. This shows that the active phase of the catalyst can be readily regenerated without any irreversible change in its structure and properties. The DRIFTS studies were also carried out at 400 and 450 °C (Fig. 7e–f). The results showed a decrease in the intensity of the bands at

Fig. 7 DRIFTS spectra obtained in the region 4000–500 cm^{-1} under different conditions: **a** room temperature in N_2, **b** at 400 °C in N_2, **c** at 400 °C in 20% O_2/Ar, **d** at 350 °C in 6.7% O_2/Ar and 13.3% C_3H_8/Ar, **e** at 400 °C in 6.7% O_2/Ar and 13.3% C_3H_8/Ar, **f** at 450 °C in 6.7% O_2/Ar and 13.3% C_3H_8/Ar



2,964, 2,903, and 2,883 cm^{-1} as well as in the 1,115–1,015 cm^{-1} region.

The activity of the catalyst **1** described in this work is comparable to the supported vanadium oxide based catalytic systems, described in the foregoing paragraph, as the conversion and selectivity is within the range reported for supported vanadium oxide catalysts. However, as compared to the Keggin compounds and V/Mg/O catalysts, catalyst **1** shows initial higher activity at a much lower temperature, 350 °C.

4 Conclusion

The new vanadium oxide based framework material **1** described here provides an active catalyst for the oxidative dehydrogenation of propane into propylene. The conversion of propane at 350 °C was 1.3% with a propylene selectivity of 36.8%. The conversion increased to 12.3% at 350 °C as the GHSV was decreased albeit at the cost of selectivity. The selectivity to propylene also decreased with increasing temperature. More detailed work is in progress to explore the potential of this class of catalysts, which are based on novel open-framework materials. Since the structures of the well-defined framework materials are fully resolved, the work offers an opportunity for a new class of ODH catalysts whose properties can potentially be modified and correlated with their structures at the molecular level. This could be helpful in preparing ODH catalysts with improved performance.

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