Oxidative dehydrogenation of propane over niobia supported vanadium oxide catalysts

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Abstract

Oxidative dehydrogenation (ODH) of propane is examined over a series of catalysts, which include Nb2O5 supported monolayer V2O5 catalysts, bulk vanadia–niobia with different vanadium oxide loadings and prepared by four different methods, V2O5 and Nb2O3. The intrinsic activity (TOF) of the samples studied indicates that vanadium containing active sites are indispensable for catalytic oxidative dehydrogenation of propane. Variations in the chemical environment of the vanadium ion do not cause significant changes in activity per site and, hence, all samples show similar TOF when the rates are normalised to the concentration of V on the surface. Selectivity to propene on the other hand strongly depends on the nature of the catalyst because readsoption and interaction of propene with the acid sites leads to total oxidation. Optimization of the weak sorption of propane is, therefore, concluded to be the key factor for the design of selective oxidative dehydrogenation catalysts.

Keywords: Niobia supported vanadium oxide catalysts; Oxidative dehydrogenation of propane

1. Introduction

Oxidative dehydrogenation (ODH) of alkanes offers an energetically attractive route for the production of alkenes. Among the various catalysts proposed for this reaction, mixed oxide catalysts containing vanadium oxide are the most frequently studied. Much of this work has focused on mixed oxides of magnesia and vanadia [1–6]. Other vanadium oxide containing mixed oxides tested include alkali and alkaline earth orthovanadates [3,7], actinide orthovanadates [8], bulk vanadia–niobia [9], VAPO-5 [10] and vanadium oxide supported on amorphous AlPO4 [11,12]. Most reports suggest that tetrahedrally coordinated vanadium favours high selectivity to alkenes, although opinions differ with respect to the exact nature of the active site. Orthovanadate [1–3], pyrovanadate [4,6] and isolated VO4 tetrahedra [5,10], are all reported to be catalytically active and selective for oxidative dehydrogenation of propane to propene.

In this contribution, the ODH of propane is examined over a series of catalysts which include Nb2O5 supported monolayer V2O5 catalysts, bulk vanadia–niobia with different vanadium oxide loadings and prepared by four different methods, V2O5 and Nb2O3. The catalysts were selected to provide a series of oxides in
which vanadium and niobium is present in different concentrations (and, hence, in different stoichiometries), and in different chemical environments. This is expected to enable conclusions to be made on the effect of the environment and the nature of the surface oxide complexes on the activity and selectivity for propane ODH.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Bulk catalysts
A series of vanadia–niobia catalysts was prepared by methods described in detail elsewhere [13]. These methods included (i) adsorption of VO(acac)₂ onto niobia from a toluene solution, (ii) coprecipitation from a mixed oxalic acid solution of niobium and vanadium using aqueous ammonia, (iii) calcination of mixed oxalates prepared by evaporating solutions of vanadium and niobium oxalates to dryness (melt method) and (iv) impregnation of niobia with NH₄VO₃. These precursors were calcined for 5 h at 630°C. The Nb₂O₅ support was obtained from the Nio- bium Products Co., USA, and was calcined at 630°C for 15 h prior to use.

2.1.2. Monolayer catalysts
For the preparation of monolayer catalysts, vanadium triisopropoxide oxide (Alfa, 95%–98% purity) was deposited onto the Nb₂O₅ support (calcined at 450–500°C, BET area 55 m² g⁻¹) by incipient wetness impregnation. The solutions of the vanadia precursor in methanol were thoroughly mixed with the oxide support and dried at room temperature in a glove box for 16 h in a nitrogen atmosphere. The impregnated samples were subsequently heated to 120°C in flowing nitrogen. The final calcination was performed in O₂ (Linde, 99.99% pure) at 450°C. For comparison, a sample of V₂O₅ (Merck) was calcined at 450°C for 5 h in flowing air.

Details of the characterization techniques used are described elsewhere [13,14].

2.2. Catalyst testing
Catalytic testing was performed using a quartz tubular downflow reactor (I.D. 4 mm) operating at atmospheric pressure. A reactant mixture of 29 vol.-% propane, 9 vol.-% O₂ and 62 vol.-% He was used. The catalyst was used in the form of grains 0.3–0.6 mm in diameter and was diluted with quartz to give a bed length of approximately 40 mm. The amount of catalyst (70–600 mg) was chosen to allow for measurements in the required conversion range. The reactor outflow was analyzed using a HP 5880A GC equipped with a TCD detector and a molecular sieve 5Å and a Heyesep Q column at 80°C.

The catalyst testing sequence involved heating the catalyst to 450°C at a rate of 15°C min⁻¹ in the reactant stream with a flow of 140 ml STP min⁻¹. This temperature was maintained for 2 h to stabilize the catalyst. Measurements were then made at 425°C with varying space velocities over a period of approximately 10 h. For the determination of the reaction orders and activation energies, measurements were made between 385 and 435°C with a maximum propane conversion below 5%. Propene oxidation experiments were carried out using a feed of 20 vol.-% propene, 6 vol.-% O₂ and 74 vol.-% He flowing at 150 ml min⁻¹. Deactivation of the catalyst was not observed during the measurements. The reaction over quartz grains was observed to be negligible.

The turnover frequency, TOF (s⁻¹), was estimated for all the catalysts by normalising the rates to the surface V and Nb atoms. The number of surface vanadium and niobium atoms for the pure vanadium, pure niobia and bulk vanadia–niobia was estimated assuming the area occupied by VO₂₅ and NbO₂₅ to be 11 and 15 Å², respectively [15,16].
Table 1
Characterisation results and catalytic activity of vanadia-niobia catalysts

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Conc. V (mol-%)</th>
<th>BET area (m² g⁻¹)</th>
<th>XRD phase a</th>
<th>Rate b (µmol/m² s)</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Surf. c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coprecipitation</td>
<td>1.14</td>
<td>8.6</td>
<td>7.6</td>
<td>T</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>1.64</td>
<td>10.3</td>
<td>7.3</td>
<td>T</td>
<td>0.093</td>
</tr>
<tr>
<td></td>
<td>2.23</td>
<td>13.9</td>
<td>6.8</td>
<td>T</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>3.15</td>
<td>15.2</td>
<td>7.4</td>
<td>T</td>
<td>0.180</td>
</tr>
<tr>
<td></td>
<td>5.23</td>
<td>18.1</td>
<td>6.8</td>
<td>T</td>
<td>0.385</td>
</tr>
<tr>
<td></td>
<td>7.12</td>
<td>20.9</td>
<td>8.2</td>
<td>T, tr B</td>
<td>0.510</td>
</tr>
<tr>
<td></td>
<td>9.05</td>
<td>21.6</td>
<td>7.2</td>
<td>T, B</td>
<td>0.291</td>
</tr>
<tr>
<td>Adsorption</td>
<td>2.15</td>
<td>12.6</td>
<td>19.9</td>
<td>T</td>
<td>0.227</td>
</tr>
<tr>
<td>Impregnation</td>
<td>1.22</td>
<td>8.51</td>
<td>9.1</td>
<td>T</td>
<td>0.137</td>
</tr>
<tr>
<td>Melt</td>
<td>1.01</td>
<td>2.6</td>
<td>38.6</td>
<td>T</td>
<td>0.038</td>
</tr>
</tbody>
</table>

a T = T-Nb₂O₅, B = β-(Nb-V)₂O₅, tr = trace.

Table 2
Characteristics of the monolayer catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET area (m²/g⁻¹)</th>
<th>V conc. (mol-%)</th>
<th>Rate a (µmol m⁻² s⁻¹)</th>
<th>TOF b (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb₂O₅</td>
<td>55</td>
<td>-</td>
<td>0.003</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.5 V₂O₅/Nb₂O₅</td>
<td>53</td>
<td>0.5</td>
<td>0.029</td>
<td>0.028</td>
</tr>
<tr>
<td>2 V₂O₅/Nb₂O₅</td>
<td>48</td>
<td>2.0</td>
<td>0.180</td>
<td>0.039</td>
</tr>
<tr>
<td>4 V₂O₅/Nb₂O₅</td>
<td>46</td>
<td>4.0</td>
<td>0.360</td>
<td>0.038</td>
</tr>
<tr>
<td>6 V₂O₅/Nb₂O₅</td>
<td>43</td>
<td>6.0</td>
<td>0.451</td>
<td>0.029</td>
</tr>
<tr>
<td>8 V₂O₅/Nb₂O₅</td>
<td>40</td>
<td>8.0</td>
<td>0.336</td>
<td></td>
</tr>
<tr>
<td>2% V₂O₅/Nb₂O₅</td>
<td>6.8</td>
<td>13.9 f (38.4 f)</td>
<td>0.167</td>
<td>0.018</td>
</tr>
</tbody>
</table>

a Rate of propane consumption per unit surface area.
b Calculated assuming all vanadium is on the surface (for Nb₂O₅ the number of Nb atoms on the surface).
c Vanadium loading greater than experimental monolayer loading.
d Bulk V₂O₅/Nb₂O₅ catalyst.
e Surface V concentration determined by XPS.
f Surface V concentration determined by LEIS.

3. Results and discussion

The physico-chemical characteristics of bulk vanadia-niobia catalysts are compiled in Table 1. For the coprecipitated catalysts, the surface concentration of vanadium increased in parallel to the bulk vanadium concentration. The surface concentration of vanadia for a particular bulk concentration in fresh catalysts, however, was also influenced by the preparation method. For example, the melt and coprecipitated catalysts with a bulk vanadium content of about 1 mol-% had surface vanadium concentrations of 2.6 and 8.6 mol-%, respectively. This is even more visible if the concentrations are normalised to BET surface areas of the catalysts. Thus, the preparation method influences drastically the surface concentration of vanadia.

The different preparation methods also led to different specific surface areas. The coprecipitated vanadia-niobia samples, for example, had a specific surface area of 7–10 m² g⁻¹ while catalysts prepared by adsorption and impregnation had 19 m² g⁻¹ and melt catalysts 39 m² g⁻¹.

Increasing concentration of vanadium (above 7 mol-%) led to a new vanadium containing phase β-(Nb-V)₂O₅, as seen by XRD measure-
ments. However, solid state $^{51}$V MAS NMR measurements [17] showed that even in the case of samples containing low vanadia (up to 7 mol-%) vanadium exists in three different coordinations, i.e., in isolated tetrahedra, corner sharing dimeric tetrahedra and distorted octahedra. This allows to conclude that $\beta$-(Nb–V)$_2$O$_5$, which contains isolated V tetrahedra, is also present at much lower concentrations. The distorted octahedra and the dimeric vanadia species correspond to vanadium ions replacing niobium ions in niobia and free vanadia species, respectively. Thus, formation of the new phase occurs already at rather low concentrations. Niobia was present as an orthorhombic phase represented in literature as T-Nb$_2$O$_5$.

The physico-chemical characteristics of the monolayer catalysts are compiled in Table 2.
The results of the characterization of the monolayer vanadium oxide catalysts by Raman spectroscopy were previously reported in detail [14]. Raman bands due to crystalline $V_2O_3$ were not observed below a vanadia loading of 7%. Thus, the monolayer loading of surface vanadia was concluded to correspond to approximately 7%. The Raman spectra changed with the vanadium oxide coverage indicating the presence of isolated tetrahedral (low and high coverage) and polymeric (high coverage) surface vanadium oxide species [14]. Compound formation of a small part of the surface vanadium oxide species with the $Nb_2O_3$ support could not be excluded in these samples.

The most important data with respect to the catalytic properties of fresh samples are compiled in Fig. 1, Fig. 2, and Fig. 3 and in Tables 1 and 2. Fig. 1 shows the propene yields of the various vanadia–niobia bulk catalysts as a function of propane conversion. Note that for a given temperature all catalysts show an identical dependence of the propene yield upon the level of conversion. In contrast, the results obtained by Chaar et al. [2] do not indicate similar trends for V–Mg–O and $V_2O_5$ catalysts. Thus, despite the fact that each point in Fig. 1 corresponds to a different catalyst and that the data include catalysts that were prepared by different methods, with different vanadium loadings and containing different phases, the intrinsic surface chemistry seems to be identical. This strongly suggests that either propane ODH is insensitive to the surface structure of the catalyst or that under reaction conditions all the catalysts have nearly identical surface structures. The latter possibility would imply a quasi equilibrium between the catalyst phases and the existence of only one type of catalytically active site (or array of surface atoms).

Earlier studies on the ODH of propane have emphasized the importance of the V–O bonding on the catalytic activity. If the catalyst surface under reaction conditions corresponds to the surface characteristics at ambient temperature, this then is in contradiction to the model proposed here. The TOF for propane conversion for the various catalysts shown in Table 1 also supports the conclusion that rate of propane oxidation is insensitive to variations in the chemical environment of the active vanadium ion. Only minor variation in rate per surface vanadium site is observed. As outlined in the introduction, however, the concentration of these active sites and, hence, the catalytic activity per unit surface area of catalyst (see Table 1) varies with the chemical composition of the catalyst. This results in different propane conversions.

![Fig. 3](image_url)  
**Fig. 3.** Propene yield as a function of propane conversion at 425°C for $Nb_2O_3$ (○), $V_2O_5$ (■), bulk 2.2%$V_2O_5/Nb_2O_3$ (●), and $Nb_2O_3$ supported $V_2O_5$ with 0.5 (□), 2 (●), 6 (▲) and 8%$V_2O_5$ (△). All data points are at O$_2$ conversions < 95%. Dotted line indicates 100% selectivity.
over the catalysts studied. It is this variation in conversion that causes the variations in selectivity.

In turning to the supported vanadium oxide catalysts, the catalytic activity per unit surface area was two orders of magnitude greater than that of the support alone (see Table 2). Vanadium is, therefore, concluded to be primarily responsible for the high catalytic activity. The rate of propane ODH per unit surface area increases first linearly with vanadia loading until 6% and then remains constant. This indicates that a monolayer loading of vanadia on niobia is reached at this point. Again the variation in the TOF’s is small among the vanadium containing samples (between 0.028 and 0.039 s⁻¹). The rate of reaction seems to be determined only by the concentration of accessible vanadia and the amount of propane sorbed (for details see Refs. [2,9]). The active site for propane ODH in the vanadia/nioibia system is, thus, concluded to contain a vanadium cation, which is shown by solid state NMR [17] and Raman spectral studies [14], to be present in a variety of stoichiometries at the surface.

Contact time variation experiments have previously shown that the main (consecutive) reaction reducing the selectivity is the sequential oxidation of propene. Thus, any means to reduce the interaction of propene with the catalyst surface inducing a lower concentration or residence time will be beneficial. Fig. 2 illustrates the improved selectivity for propene (for a given conversion) at a higher reaction temperature which is mainly attributed to the decreased surface coverage of propene at elevated temperatures. This increased selectivity for propene at higher temperatures has also been observed by Chaar et al. [2]. Similarly, the decreasing apparent energy of activation for propene oxidation among various catalysts, i.e., 6V₂O₅/Nb₂O₅ (monolayer catalyst) 157 kJ/mol, 1.5% V₂O₅/Nb₂O₅ (bulk catalyst) 128 kJ/mol, V₂O₅ 118 kJ/mol and the parallel decrease in selectivity to propene (see Fig. 3) indicates a parallel variation in the heat of adsorption of propene and the selectivity. It is speculated that the high apparent energy of activation is primarily a sign of the lower heat of adsorption and, hence, of the lower acidity of the material. Most likely the preparation of the monolayer catalysts reduces more effectively the concentration of strong Lewis acid sites than any of the other methods chosen. This explanation is in line with the suggestions of Kung and coworkers [1,2,8] that it is the basic nature of the MgO support that reduces the strength in the propene sorption and enhance the selectivity in V–Mg–O catalysts.

4. Conclusions

The intrinsic activity (TOF) of the samples studied indicates that vanadium containing active sites are indispensable for catalytic oxidative dehydrogenation of propane. All samples show similar TOF when the rates are normalised to the concentration of V on the surface. Either the variations in the chemical environment of the vanadium ion does not cause significant changes in activity per site and, therefore, the reaction is insensitive to these changes or under reaction conditions all catalysts form in equilibrium rather similar surface structure. Selectivity to propene on the other hand strongly depends on the nature of the catalyst because readsoption and interaction of propene with the acid sites leads to total oxidation. Optimization of the weak sorption of propene is, therefore, concluded to be the key factor for the design of selective oxidative dehydrogenation catalysts.

References