Effects of molybdena on the catalytic properties of vanadia domains supported on alumina for oxidative dehydrogenation of propane

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Abstract

The oxidative dehydrogenation (ODH) of propane was investigated on vanadia dispersed on alumina containing a nominal polymolybdate monolayer (4.8 Mo/nm²). Dehydrogenation rates and selectivities on these catalysts were compared with those on vanadia domains dispersed on alumina. At a given vanadia surface density, ODH reaction rates per gram of catalyst were about 1.5–2 times greater on MoOₓ-coated Al₂O₃ than on pure Al₂O₃ supports. The higher activity of vanadia dispersed on MoOₓ-coated Al₂O₃ reflects the greater reducibility of VOₓ species as a result of the replacement of V–O–Al with V–O–Mo bonds. The MoOₓ interlayer also increased the alkene selectivity by inhibiting propane and propene combustion rates relative to ODH rates. This appears to reflect a smaller number of unselective V₂O₅ clusters when alkoxide precursors are used to disperse vanadia on MoOₓ/Al₂O₃ as compared to the use of metavanadate precursor to disperse vanadia on pure Al₂O₃. At 613 K, the ratio of rate coefficients for propane combustion and propane ODH was three times smaller on MoOₓ/Al₂O₃ than on Al₂O₃ supports. The ratio of rate constants for propene combustion and propane ODH decreased by a similar factor.

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1. Introduction

Oxidative dehydrogenation (ODH) of propane to propene is an attractive alternative to nonoxidative routes, because ODH reactions are favored by thermodynamics even at low temperatures and do not lead to the formation of coke and lower molecular weight products. Among the many materials examined as catalysts for propane ODH, vanadia- and molybdena-based materials remain among the most effective [1–15]. Investigations of propane ODH on Al₂O₃- and ZrO₂-supported VOₓ and MoOₓ have shown that the highest specific activity (per V or Mo atom) for C₃H₈ ODH is achieved at near-monolayer coverages of polyvanadate (7.5 V/nm²) or polymolybdate (4.8 Mo/nm²) species on these supports [12–15]. UV–visible studies of supported vanadia and molybdena domains have shown that there is a strong correlation between the specific activity for ODH and the absorption-band-edge energy. For each oxide, the reaction turnover rate increases as the absorption-edge energy decreases. This trend is related mechanistically to the redox cycles involving lattice oxygen responsible for propane ODH [15]. Consistent with this picture, it is observed that for a given equivalent submonolayer surface coverage of the support, the propane ODH activity for dispersed vanadia is higher than that for dispersed molybdena. At oxide coverages above a monolayer, the specific activity of both oxides decreases because an increasing fraction of the deposited oxide is present within three-dimensional particles, and, hence, some of the Mo and V atoms are inaccessible for catalysis.

The effects of oxide coverage on the selectivity to propene can be described in terms of the following reaction scheme [1,3,4,9–11,13,14]:

\[
\begin{align*}
C_3H_8 & \xrightarrow{k_1} C_3H_6 \\
& \xrightarrow{k_2} CO_2 \\
& \xrightarrow{k_3} \text{other products}
\end{align*}
\]

The rate coefficients \( k_1 \), \( k_2 \), and \( k_3 \) describe the rates of propane ODH, propane combustion, and propene combustion, respectively. Values of these coefficients can be obtained by analysis of reaction rates as a function of reactant...
space velocity [7,10,13,14]. Studies of alumina-supported molybdena have shown that both \(k_2/k_1\) and \(k_3/k_1\) ratios decreased as the surface density of molybdena increased, suggesting that the presence of Mo–O–Al surface sites favors the adsorption of propene and the combustion of the resulting alkoxydes [13]. In contrast with molybdena, the values of \(k_2/k_1\) and \(k_3/k_1\) ratios on alumina-supported vanadia increased with increasing oxide surface coverage, apparently as a result of lower selectivity on three-dimensional vanadia clusters than on monomers and two-dimensional oligomers [14]. Thus, while monolayer coverage of alumina by vanadia results in high specific propane ODH activity, it also leads to lower propene selectivities.

The preceding discussion suggests that in order to attain high propane ODH activity and selectivity, the reducibility of vanadia must be increased while minimizing the formation of V\(_2\)O\(_5\) crystallites, which lead to low propene selectivity. An approach to achieve this goal is to disperse VO\(_x\) in small domains on an oxide that is less reducible than vanadia, but more reducible than the alumina support (e.g., V\(_2\)O\(_5\)/MoO\(_3\)/Al\(_2\)O\(_3\)). While Gao and co-workers [16–18] have reported higher methanol oxidation rates on bilayer V\(_2\)O\(_5\)/TiO\(_2\)/SiO\(_2\) and V\(_2\)O\(_5\)/ZrO\(_2\)/SiO\(_2\) structures than on V\(_2\)O\(_5\)/SiO\(_2\), to the best of our knowledge, similar catalysts have not been examined for alkane ODH. The most relevant previous study is by Ueda et al. [19], who have investigated bulk V–M–O mixed metal oxides (M = Al, Fe, Cr, and Ti) as ethane ODH catalysts; these authors did not explore similar compositions as bilayer oxide structures. Here, we report the preparation and structural characterization of vanadia dispersed on a monolayer of molybdena on alumina and the activity and selectivity of such materials for propane ODH. We show that a molybdena interlayer enhances ODH activity of dispersed vanadia and also suppresses propane and propene combustion side reactions.

2. Experimental

The 10.5 wt% V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) and 12 wt% MoO\(_3\)/Al\(_2\)O\(_3\) catalysts were prepared by incipient wetness impregnation of \(\gamma\)-Al\(_2\)O\(_3\) (Degussa, AG, 100 m\(^2\)/g) with a solution of ammonium metavanadate (Aldrich, 99%) and oxalic acid (NH\(_4\)VO\(_3\)/oxalic acid 1:2 molar ratio) and ammonium heptamolybdate (Aldrich, 99%), respectively. The samples were dried overnight at 398 K before thermal treatment at 573 K in a flow of dry air (Airgas, zero grade) for 3 h. Samples with 2–18 wt% V\(_2\)O\(_5\) deposited on a 12 wt% MoO\(_3\)/Al\(_2\)O\(_3\) sample were prepared using previously described methods [16]. After thermal treatment, the 12% MoO\(_3\)/Al\(_2\)O\(_3\) sample was dried at 393 K for 1 h and then transferred into a N\(_2\)-purged glove box. It was then impregnated with a solution of vanadyl isopropoxide (Aldrich, 98%) in isopropanol, kept in the glove box overnight, and transferred into a quartz tube. This procedure was used to avoid hydrolysis of the alkoxide by ambient moisture. These samples were treated in flowing N\(_2\) at 393 K for 1 h, then at 573 K for 1 h, subsequently treated in flowing dry air at 573 K for 1 h, and finally at 773 K for 2 h. The samples were pressed into wafers, crushed, and sieved to retain particles with 0.18–0.36 mm diameters. Vanadyl isopropoxide was chosen as the vanadium precursor because it led to a higher dispersion of vanadia than by aqueous impregnation of 12 wt% MoO\(_3\)/Al\(_2\)O\(_3\) with ammonium vanadate. BET surface areas were measured using nitrogen physisorption at its normal boiling point and a Quantasorb surface analyzer (Quantachrome Corp.). Raman spectra were recorded at ambient temperature using a rotating stage quartz cell after samples were treated in dry air at 723 K for 1 h within the cell [13,14].

Propane ODH rates were measured in a quartz microreactor using 0.02–0.04 g of catalyst diluted with equal amounts of quartz powder (40–80 mesh) in order to minimize temperature gradients. Propane (Airgas, 99.99%) and O\(_2\) (Airgas, 99.999%) were used as reactants and He (Airgas, 99.999%) was used as an inert diluent. The partial pressure of propane was 13.5 kPa and that of oxygen, 1.7 kPa, and rate measurements were carried out at 583–703 K. The effluent from the reactor was analyzed with a Hewlett-Packard 6890 gas chromatograph [7,8]. Reactor residence times were varied by changing the reactant flow rates; the resulting propane and oxygen conversions were kept below 2% and 20%, respectively, in all experiments.

3. Results and discussion

BET surface areas and nominal MO\(_x\) (M = V, Mo) surface densities are shown in Table 1 for all samples. MO\(_x\) surface densities are reported as the number of M atoms per BET surface area (M/\(\text{nm}^2\)). Two-dimensional MO\(_x\) oligomers form a monolayer on Al\(_2\)O\(_3\) at 7.5 V/\(\text{nm}^2\) [20] and 4.8 Mo/\(\text{nm}^2\) [21–23]. The sample designated as 12Mo/Al and used as the coated support has a Mo surface density of 4.8 Mo/\(\text{nm}^2\), corresponding to an equivalent poly-molybdate monolayer. The addition of vanadia to the surface of 12Mo/Al monotonically decreased BET surface areas. However, most of the observed change is merely due to the increase in catalyst mass upon addition of vanadia. When the BET area was calculated on the basis of the amount of support, Table 1 shows that the decrease in surface area with addition of vanadia is significantly smaller. The sample designated as 10V/12Mo/Al has an apparent surface density of 7.5 V/\(\text{nm}^2\), which corresponds to an equivalent polyvanadate monolayer on Al\(_2\)O\(_3\). The dispersion of vanadia directly onto alumina causes a reduction in the BET surface area similar to that observed when vanadia is dispersed onto a monolayer equivalent of molybdena on alumina. The sample designated as 10.5V/Al also has an apparent vanadium surface density corresponding to about one polyvanadate monolayer (7.5 V/\(\text{nm}^2\)).

The Raman spectra of samples treated in dry air at 723 K for 1 h are shown in Fig. 1. The spectrum of 10.5V/Al
Table 1
Surface areas and MO\textsubscript{x} (M = V or Mo) surface densities of catalysts

<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>Catalyst name</th>
<th>Surface area (m\textsuperscript{2}/g\textsubscript{cat})</th>
<th>Surface area (m\textsuperscript{2}/g\textsubscript{support}\textsuperscript{a})</th>
<th>V\textsubscript{x} surface density (V/\text{nm}\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>12Mo/Al</td>
<td>104</td>
<td>–</td>
<td>4.8 (Mo/\text{nm}\textsuperscript{2})</td>
</tr>
<tr>
<td>10.5 wt% V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>10.5V/Al</td>
<td>92</td>
<td>–</td>
<td>7.6</td>
</tr>
<tr>
<td>2 wt% V\textsubscript{2}O\textsubscript{5}/12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>2V/12Mo/Al</td>
<td>108</td>
<td>110</td>
<td>1.2</td>
</tr>
<tr>
<td>4 wt% V\textsubscript{2}O\textsubscript{5}/12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>4V/12Mo/Al</td>
<td>104</td>
<td>108</td>
<td>2.5</td>
</tr>
<tr>
<td>6 wt% V\textsubscript{2}O\textsubscript{5}/12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>6V/12Mo/Al</td>
<td>98</td>
<td>104</td>
<td>4.1</td>
</tr>
<tr>
<td>8 wt% V\textsubscript{2}O\textsubscript{5}/12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>8V/12Mo/Al</td>
<td>93</td>
<td>101</td>
<td>5.7</td>
</tr>
<tr>
<td>10 wt% V\textsubscript{2}O\textsubscript{5}/12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>10V/12Mo/Al</td>
<td>88</td>
<td>98</td>
<td>7.5</td>
</tr>
<tr>
<td>12 wt% V\textsubscript{2}O\textsubscript{5}/12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>12V/12Mo/Al</td>
<td>78</td>
<td>89</td>
<td>10.2</td>
</tr>
<tr>
<td>18 wt% V\textsubscript{2}O\textsubscript{5}/12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>18V/12Mo/Al</td>
<td>70</td>
<td>85</td>
<td>17.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Support = 12 wt% MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}.

Fig. 1. (a) Raman spectra of 12Mo/Al, 10.5V/Al, and xV/12Mo/Al (x = 2–18). (b) Raman spectra of a monolayer of vanadia dispersed on 12Mo/Al, prepared from VO(O\textsubscript{iPr}) and NH\textsubscript{4}VO\textsubscript{3}.

shows a broad band at \(\sim 1040\) cm\textsuperscript{-1} characteristic of isolated monovanadate species, a broad band in the region of 700–950 cm\textsuperscript{-1} characteristic of polyvanadate species, and weaker bands at 1000, 708, 535, 488, and 412 cm\textsuperscript{-1} arising from V\textsubscript{2}O\textsubscript{5} crystallites [14,24–28]. In view of the much larger Raman scattering cross section of crystalline V\textsubscript{2}O\textsubscript{5} relative to dispersed monovanadate and polyvanadate structures [28], we conclude that these samples contain only traces of crystalline V\textsubscript{2}O\textsubscript{5}.

The dehydrated 12Mo/Al sample shows a broad band at 1016 cm\textsuperscript{-1}, a weaker band at 822 cm\textsuperscript{-1}, and a broad feature at 673 cm\textsuperscript{-1}. Previous studies of MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} samples have assigned bands at 955–1010 cm\textsuperscript{-1} to MoO\textsubscript{x} oligomers and bands at 999, 822, and 673 cm\textsuperscript{-1} to MoO\textsubscript{3} crystallites [13,29–31]. Since the Raman cross section for MoO\textsubscript{3} is larger than that for monovanadate and polyvanadate species, these data indicate that most of the molybdena covers the surface of the alumina. The deposition of vanadia onto 12Mo/Al leads to Raman bands characteristic of various vanadia structures for vanadia contents higher than 2 wt% (> 1.2 V/\text{nm}\textsuperscript{2}) (Fig. 1a). The band at 1040 cm\textsuperscript{-1} corresponds to V=O vibrations in isolated monovanadate species. For 4V/12Mo/Al, a well-defined band appears at 775 cm\textsuperscript{-1}, which is assignable to either V–O–V vibrations of polyvanadate species [24,25,32], or possibly to V–O–Mo vibrations for polymolybdovanadate species [33,34]. For 6 wt% vanadia and higher (> 4.1 V/\text{nm}\textsuperscript{2}), bands are detected at 1000, 708, 535, 488, and 415 cm\textsuperscript{-1} due to crystalline V\textsubscript{2}O\textsubscript{5}. The fraction of V present as V\textsubscript{2}O\textsubscript{5} is less than a few percent, based on the relative scattering cross sections of V\textsubscript{2}O\textsubscript{5} and monovanadate and polyvanadate species [28].

The influence of precursor composition on the structure of dispersed vanadia is shown in Fig. 1b. Both spectra in Fig. 1b are for samples with vanadia loadings equivalent to one monolayer (7.5 V/\text{nm}\textsuperscript{2}) dispersed on 12Mo/Al, prepared using VO(O\textsubscript{iPr}) and NH\textsubscript{4}VO\textsubscript{3}. The principal bands seen in the sample prepared using NH\textsubscript{4}VO\textsubscript{3} are those characteristic of V\textsubscript{2}O\textsubscript{5} (1000, 708, 535, 488, and 413 cm\textsuperscript{-1}), which are absent from the spectrum of the sample prepared using NH\textsubscript{4}VO\textsubscript{3}. In contrast, the sample prepared using the isopropoxide precursor shows stronger features for monovanadate (the band at 1040 cm\textsuperscript{-1}) and either polyvanadate or polymolybdovanadate species (the band at 775 cm\textsuperscript{-1}), and weaker features...
for $V_2O_5$. These results suggest for a given apparent surface density of vanadia, a greater fraction of the vanadia is dispersed in the form of monovanadate and polyvanadate species, and that structures involving $V-O-Mo$ bonds may be formed when vanadyl isopropoxide is used as the vanadium precursor.

Temperature-programmed reduction (TPR) data were used in order to probe the effects of the MoO$_x$ interlayer on vanadia reducibility and the results are shown in Fig. 2. The data for 12Mo/Al show a single reduction peak centered at about 710 K followed by a broad feature at higher temperatures. These data are similar to those previously reported [13,15]. The peak at 710 K corresponds to the reduction of Mo$^{6+}$ to Mo$^{4+}$, whereas the feature at higher temperatures reflects the reduction of Mo$^{4+}$ to Mo$^0$ [35,36]. TPR of 10.5V/Al led to a broad asymmetric feature at about 710 K, which has been previously attributed to the reduction of V$^{5+}$ to V$^{3+}$ [15]. The addition of increasing amounts of vanadia to 12Mo/Al leads to a broadening of this feature and its shape evolves to one resembling that in 10.5V/Al. Above 8 wt% (> 5.7 V/nm$^2$) vanadia contents, a sharp feature appears at ~ 690 K, which shifts to 720 K with increasing vanadia content. This new feature is attributed to the reduction of increasingly larger amounts of crystalline $V_2O_5$ [14].

The logarithm of the initial rate of H$_2$ reduction is plotted in Fig. 1b versus inverse temperature. For a fixed temperature, it is apparent that 12Mo/Al exhibits the lowest reduction rate and that reduction rates increase with increasing vanadia contents up to 10 wt% (7.5 V/nm$^2$). At higher contents, reduction rates decreased, apparently because of the lower accessibility of V atoms and the longer oxygen diffusion distances prevalent in larger three-dimensional structures. It is also evident that the rate of reduction of 10V/12Mo/Al is significantly higher than for 10.5V/Al or 12Mo/Al. These trends are qualitatively similar to those reported by Ruth et al. [37], who showed that the initial reduction temperature for bulk $V_2O_5$, MoO$_3$, and Mo$_6$V$_9$O$_{40}$ increases in the order Mo$_6$V$_9$O$_{40}$ (748 K) < $V_2O_5$ (773 K) < MoO$_3$ (848 K). Thus, it is possible that the increase in catalyst reducibility observed when VO$_x$ is dispersed on 12Mo/Al is attributable to the formation of polymolybdovanadate species. Such an interpretation would be consistent with the assignment of the Raman band at 775 cm$^{-1}$ to $V-O-Mo$ vibrations (see above).

Fig. 3 shows C$_3$H$_6$ and CO$_x$ (CO + CO$_2$) selectivities on 10.5V/Al and 10V/12Mo/Al as a function of C$_3$H$_8$ conversion at 613 and 673 K. On both catalysts, C$_3$H$_6$ selectivity decreases and CO$_x$ selectivity increases with increasing C$_3$H$_8$ conversion over the range of C$_3$H$_8$ conversions investigated. For a given C$_3$H$_8$ conversion, 10.5V/12Mo/Al gives higher C$_3$H$_6$ selectivities than 10.5V/Al. These data show that the dispersion of vanadia on a layer of MoO$_x$ deposited on Al$_2$O$_3$ increases the ODH selectivity of active vanadia domains. These selectivity effects are discussed later in terms of the rate constants for ODH and for primary and secondary combustion reactions.

The initial rate of propene formation (at zero propane conversion) was determined by extrapolation of propene formation rates to zero residence times [7,9–11,13,14]. Fig. 4a shows the effects of VO$_x$ surface density on initial propene formation rates (per catalyst mass) at 613, 643, and 673 K. At each temperature, initial propene formation rates increased with increasing V surface density up to values of ~ 7–8 V/nm$^2$, corresponding to a theoretical polyvanadate monolayer, and then decreased at higher surface densities. Propene formation rates on 10.5V/Al are also shown in Fig. 4a. These data clearly show that propene formation rates are significantly higher when VO$_x$ structures are deposited on a MoO$_x$-modified Al$_2$O$_3$ surface than when similar structures are placed on pure Al$_2$O$_3$ at apparent V surface densities corresponding to a theoretical monolayer. Areal propene formation rates (based on BET surface area) are shown in
Fig. 3. Dependence of C$_3$H$_6$ and CO$_x$ selectivities as functions of C$_3$H$_8$ conversion for (a) 613 K and (b) 673 K.

Fig. 4b. Above 10 VO$_x$/nm$^2$, areal rates reach nearly constant values, indicating that neither the specific activity nor the amount of exposed VO$_x$ species increased as VO$_x$ surface densities exceed theoretical polyvanadate monolayer values.

Fig. 5a shows initial propene formation rates normalized per V atom as a function of V surface density. Since the rate of propene formation on 12Mo/Al is very small at the temperatures of the present study, no correction was made to separate the rate of propene formation on exposed MoO$_x$ from that on VO$_x$. At all three temperatures, rates (per V atom) reached maximum values at surface densities of $\sim$ 7–8 VO$_x$/nm$^2$, as also shown previously for V$_2$O$_5$/Al$_2$O$_3$ [28]. At a given V surface density, propene formation rates are 1.5–2.0 times higher when VO$_x$ is dispersed on MoO$_3$/Al$_2$O$_3$ instead of on pure Al$_2$O$_3$. The trends shown for high surface densities in Fig. 5 are consistent with the expected loss of accessibility of V centers as three-dimensional V$_2$O$_5$ structures form at apparent VO$_x$ surface densities above 7.5 V/nm$^2$ (see Figs. 1 and 2).

The observed increase in specific rates with V surface density below 7.5 V/nm$^2$ reflects a monotonic increase in the size and reducibility of VO$_x$ domains [15]. The UV–visible edge energy of V$_2$O$_5$/Al$_2$O$_3$ samples decreases with increasing V surface density, as a result of electron delocalization over larger VO$_x$ domains containing V–O–V linkages. The decrease in UV–visible band-edge energy is also indicative of a greater ease of O-to-V electron transfer, a critical step in the oxidative addition of propane to vanadia structures. Since this step has been shown to be rate limiting, increasing its rate would also increase the rate of propane ODH. Fig. 1a shows a similar pattern in the change in the structure of the dispersed VO$_x$ with increasing vanadia loading for vanadia dispersed on alumina containing a layer of molybdena as that reported for vanadia dispersed on alumina [15]. The most significant difference is the appearance of the band at 775 cm$^{-1}$, which grows in intensity with increasing vanadia loading. As noted earlier, the concurrent increase in the rate of H$_2$ reduction of vanadia deposited...
on layers of molybdena deposited on alumina relative to that for vanadia deposited on alumina suggests that both the band at 775 cm$^{-1}$ and the increased rate of reduction can be attributed to the formation of V–O–Mo bonds associated possibly with polymolydovanadate species. This conclusion is supported by the results presented in Fig. 6, which show that the rate of H$_2$ reduction (per gram or per V atom) at 613 K for x V/M12Mo/Al increases with VO$_x$ surface density up to a value of 7.5 V/nm$^2$ and then decreases. This pattern is similar to that seen in Figs. 4a and 5 for propene formation rates. It is also observed that at a surface density of 7.5 V/nm$^2$, the rate of VO$_x$ reduction for vanadia supported on alumina is significantly lower than that for vanadia supported on alumina containing a monolayer of molybdena. This effect of the molybdena interlayer is consistent with the expected reducibility of V–O–Mo bonds compared to V–O–Al bonds.

Fig. 7a shows initial propene selectivities as a function of V surface density. At the three reaction temperatures used the initial propene selectivity is $\sim 95\%$ on the 12Mo/Al material used as the support. Initial selectivities increased to 100% with the addition of small amounts of V, but then decreased monotonically for V surface densities above 2 VO$_x$/nm$^2$. At 643 and 673 K, the MoO$_x$ interlayer did not influence initial propene selectivities, but this MoO$_x$ interlayer, however, increased propene selectivities at 613 K. Fig. 7b demonstrates that V surface density effects are virtually identical for VO$_x$ domains dispersed on Al$_2$O$_3$ and MoO$_x$/Al$_2$O$_3$ supports, but the latter give higher initial propene selectivities than Al$_2$O$_3$ supports at 613 K for all surface densities.

Previous kinetic and mechanistic studies of propane ODH on VO$_x$ and MoO$_x$ catalysts have shown that primary and secondary reactions can be accurately described by the scheme \cite{1,3,4,7,9-11,13,14}:

$$
\begin{align*}
\text{C}_3\text{H}_8 & \quad \xrightarrow{k_1} \quad \text{C}_3\text{H}_6 \\
\text{C}_3\text{H}_6 & \quad \xrightarrow{k_2} \quad \text{CO}_x
\end{align*}
$$
Each reaction is accurately described using pseudo-first-order dependencies on propane and propene reactants and zero order in O₂ [7,10,11]. The propane ODH rate constant \( k_1 \) is given by the initial propene synthesis rates (extrapolated to zero residence time, \( \tau \)). The direct combustion rate constant \( k_2 \) is obtained from the \( \text{C}_3\text{H}_6 \) selectivity extrapolated to zero space time \( (S^0 = k_1/(k_1 + k_2)) \). Finally, propene combustion rate constants \( k_3 \) are estimated from the measured effects of space time on propene selectivity \( (S = S^0[1 - (k_3 + k_2 + k_1)C_v\tau/2], \) where \( C_v \) is the concentration of M atoms per unit reactor volume). The \( k_2/k_1 \) and \( k_3/k_1 \) ratios reflect relative rates of \( \text{C}_3\text{H}_6 \) combustion and dehydrogenation, and of \( \text{C}_3\text{H}_6 \) combustion and dehydrogenation, respectively. Small values of these ratios lead to higher propene selectivities at a given propane conversion. The \( k_2/k_1 \) ratios are typically small (0.1–0.2) [7–11,13,14] and propene selectivities and yields depend mostly on the value of \( k_3/k_1 \) ratios.

Fig. 8 shows \( k_2/k_1 \) ratios as a function of VOₓ surface density. These ratios decrease with increasing VOₓ surface density up to \( \sim 2 \) V/nm² and then increase monotonically for higher surface densities. The presence of a molybdena interlayer has no effect on the value of \( k_2/k_1 \) at 673 K, but leads to a lower value of this ratio at lower temperatures (Fig. 8a). On all catalysts, \( k_2/k_1 \) ratios increased with increasing reaction temperature, indicating that the activation energy for propane combustion is higher than for ODH [14]. The \( k_2/k_1 \) ratios increased with increasing V surface density on both supports, but they were significantly lower on MoOₓ/Al₂O₃ than on pure Al₂O₃ supports at all surface densities (Fig. 8b).

The influence of vanadia surface density on \( k_3/k_1 \) ratios is shown in Fig. 9a for MoOₓ/Al₂O₃ supports. The \( k_3/k_1 \) ratios decrease with increasing surface density up to 7.5 VOₓ/nm², and then increase gradually as \( \text{V} \) surface densities increases beyond this value. With increasing temperature, \( k_3/k_1 \) decreases, indicating that the activation energy for propane ODH is larger than that for propene ODH. These \( k_3/k_1 \) values are much lower for VOₓ domains supported on MoOₓ/Al₂O₃ than for domains supported at similar sur-
lower $k_3/k_1$ ratios than when dispersed on $\text{Al}_2\text{O}_3$ at all $\text{VO}_x$ surface densities. This appears to reflect the higher dispersion of $\text{VO}_x$ species on $\text{MoO}_x/\text{Al}_2\text{O}_3$ supports than on $\text{Al}_2\text{O}_3$, which minimizes unselective reactions prevalent in $\text{V}_2\text{O}_5$ crystallites. These unselective reactions lead to the observed increase in $k_3/k_1$ ratios with increasing $\text{VO}_x$ surface densities on both $\text{MoO}_x/\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ supports. This interpretation is consistent with the observation of an increasing amount of $\text{V}_2\text{O}_5$ in the Raman spectra shown in Fig. 1a.

4. Conclusions

The dispersion of $\text{VO}_x$ on alumina containing a monolayer equivalent of molybdena increases the catalyst activity (per V atom) and selectivity for propane ODH to propene. The higher activity is ascribed to the formation of $\text{V–O–Mo}$ bonds between the dispersed vanadia and the molybdena layer. The formation of these bonds appears to be facilitated by the use of vanadyl isopropoxide as the precursor for the dispersed vanadia. Analysis of the reaction kinetics shows that the ratios of the rate coefficients for propane and propene combustion relative to propane ODH are significantly lower for vanadia supported on a monolayer of molybdena on alumina than those for vanadia supported on alumina alone. These results are unexpected and may be attributable to the presence of $\text{V–O–Mo}$ bonds formed by reaction of the dispersed vanadia with the molybdena layer deposited on the alumina support. It is possible that these bonds are associated with the formation of polyvanadobisvanadate species.

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References