The structure and catalytic properties of binary dispersed oxide structures prepared by sequential deposition of VO, and MoO, or VO, and CrO, on Al,O were examined using Raman and UV-visible spectroscopies, the dynamics of stoichiometric reduction in H, and the oxidative dehydrogenation of propane. VO, domains on Al,O modified by an equivalent MoO, monolayer led to dispersed binary structures at all surface densities. MoO, layers led to higher reactivity for VO, domains present at low VO, surface densities by replacing V−O−Al structures with more reactive V−O−Mo species. At higher surface densities, V−O−V structures in prevalent polyvanadates were replaced with less reactive V−O−Mo, leading to lower reducibility and oxidative dehydrogenation rates. Raman, reduction, and UV-visible data indicate that polyvanadates predominant on Al,O convert to dispersed binary oxide structures when MoO, is deposited before or after VO, deposition; these structures are less reducible and show higher UV-visible absorption energies than polyvanadates structures on Al,O. The deposition sequence in binary Mo−V catalysts did not lead to significant differences in structure or catalytic rates, suggesting that the two active oxide components become intimately mixed. The deposition of CrO, on Al,O led to more reactive VO, domains than those deposited on pure Al,O at similar VO, surface densities. At all surface densities, the replacement of V−O−Al or V−O−V structures with V−O−Cr increased the reducibility and catalytic reactivity of VO, domains; it also led to higher propene selectivities via the selective inhibition of secondary C,H combustion pathways, prevalent in VO,−Al,O, and of C,H combustion routes that lead to low alkene selectivities on CrO,−Al,O. VO, and CrO, mix significantly during synthesis or thermal treatment to form CrVO, domains. The deposition sequence, however, influences catalytic selectivities and reduction rates, suggesting the retention of some of the component deposited last as unmixed domains exposed at catalyst surfaces. These findings suggest that the reduction and catalytic properties of active VO, domains can be modified significantly by the formation of binary dispersed structures. VO,−CrO, structures, in particular, lead to higher oxidative dehydrogenation rates and selectivities than do VO, domains present at similar surface densities on pure Al,O supports.

1. Introduction

The oxidative dehydrogenation (ODH) of propane provides an attractive route for the synthesis of propene. This reaction occurs on oxides of V, Mo, and Cr with V-based catalysts typically providing higher rates and propene selectivities. Supports influence rates and selectivities on dispersed VO, domains. For example, VO, supported on ZrO, is highly active but gives low propene selectivities, while VO,Al,O gives lower rates but much higher alkene selectivities.

ODH reactions on supported VO, catalysts involve redox cycles and kinetically relevant C−H bond activation steps that require electron transfer from O to V within VO, domains. Chen et al. showed that ODH turnover rates increase with decreasing VO, UV-visible absorption edge energies and with increasing reducibility of VO, domains in H,. ODH turnover rates increased as polyvanadates became the predominant VO, species, suggesting that linkages between monovanadate structures and support cations decrease the reactivity and reducibility of V−oxo species. These data also suggested that an intervening layer of a more reducible oxide (MoO,) may minimize these support effects by replacing V−O−support linkages with more reactive V−O−M linkages.

Few such binary dispersed oxide catalysts have been reported. Gao et al. and Liu et al. reported the catalytic properties of V,O/TiO, or VOO/Al,O for CH,OH oxidation and VOO/Al,O for CH,CH,OH oxidation, respectively. In both studies, the interven- ing layer increased the reducibility and catalytic activity of VO, domains. Such binary dispersed structures have also been examined for ODH reactions. Cherian et al. reported that VO, structures on Al,O and TiO, supported modified by CrO, gave higher rates but lower propene selectivities than catalysts containing only VO, domains on these supports. The latter study reported a single composition, without systematic examination of any structural implications and catalytic consequences of compositional changes. Dai et al. described a series of binary dispersed VO,/MoO,/Al,O catalysts prepared by dispersing VO, on Al,O modified by a nominal polymolybdate monolayer. For a given VO, surface density, active structures on MoO,-coated Al,O were more reducible than those on Al,O, apparently because less reactive V−O−Al linkages are replaced with V−O−Mo bonds; these trends were also reflected in the higher propane ODH turnover rates measured on VO, structures.

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dispersed in MoO3/Al2O3 relative to those on similar V2O5 domains on pure Al2O3 supports. MoO3 interlayers also decreased primary and secondary combustion rates and led to higher propene selectivities. In contrast, Bänares and Khatib51 found no synergistic effects in VOx–MoO3/Al2O3 samples prepared by impregnation, which contained Mo−V−O mixed phases at (Mo + V) surface densities above those required for two-dimensional oxo-oligomers on Al2O3 surfaces.

Here, we aim to probe the structure and catalytic function of binary dispersed oxide catalysts for alkane ODH reactions. Samples were prepared by dispersing VOx species on Al2O3 support surfaces modified by Mo and Cr oxides and also by preparing “inverse bilayers” in which Mo and Cr oxides are dispersed on Al2O3 modified by a polyvanadate monolayer. The resulting structures were examined by Raman and UV−visible spectroscopies and by measurements of their reduction dynamics in H2, and their catalytic function was determined by rigorous measurements of turnover rates and of rate constants for primary and secondary reactions.

2. Experimental Section


Fumed Al2O3 (Degussa AG; surface area 107 m2/g) was contacted with deionized water, dried at 383 K for 72 h, and treated in ambient air at 823 K for 3 h before use in a process intended to strengthen aggregates; its BET surface area was 125 m2/g after this treatment. MoO3/Al2O3 (MoAl) and CrO3/Al2O3 (CrAl) with various active oxide surface densities were prepared by impregnating Al2O3 with solutions of molybdenyl acetylacetonate (CrAl) with various active oxide surface densities were prepared by impregnating Al2O3 with solutions of molybdenyl acetylacetonate (Alfa Aesar, 99%) in acetone (Aldrich, 99.5%) or with aqueous solutions of chromium(III) nitrate nonahydrate (Aldrich, 98%). Samples were then dried at 383 K in ambient air overnight and treated in flowing dry air (Airgas, zero grade, 0.83 cm3 s−1) by heating to 773 K at 0.167 K s−1 and then holding at 773 K for 2 h. VOx/Al2O3 (VAl) was prepared by incipient-wetness impregnation of Al2O3 with 2-propanol (Aldrich, 99.99%) solutions of vanadyl isopropoxide (Aldrich, 98%): samples were kept in a N2 flow within a glovebox overnight and transferred into a quartz reactor sealed with stopcocks at each end. These samples were treated at 393 K in flowing N2 (Airgas, 99.999%, 1.67 cm3 s−1) for 1 h and at 573 K for 1 h; air (Airgas, zero grade, 1.67 cm3 s−1) was then introduced and samples were held at 573 K for 1 h and at 773 K for 2 h.

Binary dispersed VOx/MoO3/Al2O3 (VMoAl) and VOx/CrO3/Al2O3 (VCrAl) catalysts were prepared by incipient-wetness impregnation of MoAl or CrAl samples with 2-propanol solutions of vanadyl isopropoxide with the same procedures used for VAl. MoO3/VOx/Al2O3 (MoVAI) catalysts with varying MoO3 contents were prepared by impregnation of 10%V2O5/Al2O3 with acetone solutions of molybdenyl acetylacetone, and then treating them at 383 K in ambient air and in flowing dry air at 773 K for 2 h. A 12%Cr2O3/10%V2O5/Al2O3 (12Cr10VAI) sample was prepared by incipient-wetness impregnation of 10%V2O5/Al2O3 with aqueous chromium(III) nitrate solutions, followed by drying at 383 K in ambient air and treatment in flowing dry air at 773 K for 2 h.

2.2. Catalyst Characterization. BET surface areas were measured using Quantasorb units (Quantasorb 1 or Quantasorb 6 Surface Analyzers, Quantachrome Corp.) and N2 at its normal boiling point. Samples were treated in dynamic vacuum (0.1 Pa) at 393 K for at least 3 h before BET measurements. X-ray diffraction (XRD) data were measured with a Siemens D5000 unit at ambient temperature using Cu Kα radiation. The X-ray tube was operated at 45 kV and 35 mA, and the scan rate was 1.2°/min.

Raman spectra were collected using a Hololab Series 5000 spectrometer (Kaiser Optical) equipped with a frequency-doubled 75-mW Nd:YAG laser (532 nm). Samples were pressed into self-supported wafers (0.9 cm diameter, ~50 mg cm−2) at 200 MPa and then held onto a rotating holder within a quartz Raman cell. Raman spectra were recorded at ambient temperature before and after treating samples in flowing dry air (Airgas, zero grade, 0.83 cm3 s−1) while heating to 673 K at 0.167 K s−1 and holding at 673 K for 1 h.

Temperature-programmed reduction (TPR) studies were carried out in a flow unit (QS-10, Quantachrome Corp.). H2 concentrations were measured using a thermal conductivity detector calibrated by reducing CuO. The sample amount (15−100 mg) was chosen to maintain a constant number of removable oxygen atoms (equivalent to 5 mg of MoO3). Samples were heated to 1173 K in 20%H2−Ar (Praxair, 99.999%) at 0.167 K s−1 and held at 1173 K for 1 h. H2O reduction products were removed before thermal conductivity detection with a 13X sieve at ambient temperature.

Diffuse reflectance UV−visible spectra were collected with a Cary 4 spectrophotometer (Varian Corp.) equipped with a Harrick Scientific diffuse reflectance attachment (DRP-XXX) and an environmental chamber (DRA-2CR). Samples were treated in 20% O2−He (Praxair, 99.999%, 0.83 cm3 s−1) at 723 K for 0.5 h before measurements. The Kubelka−Munk function (F(R∞)) was used to convert reflectance data into pseudoabsorbance using MgO as a reflective standard.52,53 Absorption-edge energies were calculated from the x-intercept of a linear regression of [(F(R∞))hν]1/2 data versus hν.

2.3. Catalytic Rates and Selectivity Measurements. Oxidative dehydrogenation rates and selectivities were measured at 583−673 K using a quartz flow microreactor. The reactor is 50 cm long, and the catalyst section is 10 mm in diameter and 35 mm in length. The reactor was heated via an electrical furnace, and the temperature was set by a temperature controller (WATLOW) and measured by a K-type thermocouple inserted into the reactor and positioned within the catalyst bed. Temperature gradients were avoided by diluting catalyst samples (20−40 mg, 250−500 μm) with equal amounts of acid-washed quartz (250−500 μm). C3H8 (13.5 kPa, Airgas, 99.9%) and O2 (1.7 kPa, Airgas, 99.999%) with He as balance (Airgas, 99.999%) were used as reactants. C3H8 and O2 conversions were kept below 2% and 20%, respectively, by varying reactant flow rates. Space velocities were 30 000−500 000 cm3 g−1 h−1. Reactant and product concentrations were measured by chromatography (Hewlett-Packard 6890) using a Carboxen 1004 packed column connected to a thermal conductivity detector and HP-PLOT Q capillary column with a flame ionization detector.

Reactor residence time effects on rates and selectivities were used to estimate C3H8 dehydrogenation (r1) and combustion (r2) rates by extrapolating C3H8 and CO2 synthesis rates to zero residence time. C3H8 combustion rates (r2) were obtained from the slope of C3H8 selectivity data as a function of residence time.16−23 These primary and secondary reactions and their respective rate constants (k1, k2, k3) are shown in the scheme below:

\[ \begin{align*} 
\text{C}_3\text{H}_8 & \quad \overset{k_1}{\rightarrow} \quad \text{C}_3\text{H}_6 \\
\text{C}_3\text{H}_6 & \quad \overset{k_2}{\rightarrow} \quad \text{CO}_2 \\
\end{align*} \]

Dehydrogenation and combustion rates are assumed to be first-order in C3H8 and C3H6 and zero-order in O2, as found
TABLE 1: BET Surface Areas and VO\textsubscript{x} Surface Density of V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} Catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>wt % V\textsubscript{2}O\textsubscript{5}</th>
<th>surface area (m\textsuperscript{2}/g cat)</th>
<th>surface area (m\textsuperscript{2}/Al\textsubscript{2}O\textsubscript{3})</th>
<th>VO\textsubscript{x} surface density (V/mm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>3%VIAl</td>
<td>3.1</td>
<td>108.1</td>
<td>111.6</td>
</tr>
<tr>
<td>7%V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>7%VIAl</td>
<td>7.3</td>
<td>119.3</td>
<td>128.7</td>
</tr>
<tr>
<td>10%V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>10%VAl</td>
<td>8.3</td>
<td>103.3</td>
<td>112.6</td>
</tr>
<tr>
<td>15%V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>15VAl</td>
<td>12.4</td>
<td>94.8</td>
<td>108.3</td>
</tr>
<tr>
<td>18%V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>18VAl</td>
<td>14.8</td>
<td>91.1</td>
<td>106.9</td>
</tr>
</tbody>
</table>

*Weight loading obtained by inductively coupled plasma (ICP) analysis.

experimentally on MoO\textsubscript{x} and VO\textsubscript{x} catalysts.\textsuperscript{16–21} Values of k\textsubscript{3}/k\textsubscript{1} are calculated from primary selectivities (S\textsubscript{C-H\textsubscript{6}}\textsuperscript{0}) using

\[ S_{C,H_6}^0 = k_3/(k_1 + k_2) \]

while k\textsubscript{3} is obtained from C\textsubscript{H\textsubscript{6}} selectivities using

\[ S_{C,H_6} = S_{C,H_6}^{0}[1 - (k_1 + k_2 + k_3)C_v\tau/2] \]

where \( \tau \) is the residence time and \( C_v \) is the number of V-atoms per unit volume.\textsuperscript{17}

3. Results and Discussion

3.1. Catalyst Characterization. 3.1.1. Surface Areas and Structure of Catalysts. Surface areas and VO\textsubscript{x} surface densities for all samples, as well as their designated nomenclature, are shown in Tables 1–3. Surface areas of VAI samples decreased with increasing VO\textsubscript{x} content and surface density (Table 1), as was also found for VO\textsubscript{x} dispersed on Al\textsubscript{2}O\textsubscript{3} containing a nominal monolayer of MoO\textsubscript{3} (12MoAl) or CrO\textsubscript{3} (12CrAl). Surface areas for VMoAl and VCrAl with similar VO\textsubscript{x} surface densities but varying MoO\textsubscript{3} or CrO\textsubscript{3} contents also decreased with increasing MoO\textsubscript{3} and CrO\textsubscript{3} content (Tables 2 and 3). These changes in surface areas merely reflect the larger total mass of samples per amount of Al\textsubscript{2}O\textsubscript{3} in each sample; surface areas per amount of Al\textsubscript{2}O\textsubscript{3} (Tables 1–3) are essentially the same in all samples. Thus, dispersing active oxides, as monolayers or bilayers, does not influence Al\textsubscript{2}O\textsubscript{3} surface area.

Figure 1 shows X-ray diffraction data for selected samples. Pure Al\textsubscript{2}O\textsubscript{3} shows only lines for its \( \gamma \)-phase, which is the only phase detected in 10VAl, 12MoAl, and 12CrAl. 10V12MoAl and 12Mo10VAl showed lines for AlVMO\textsubscript{7} and weaker lines for VMO\textsubscript{7}. 10V12CrAl showed lines for AlVCrO\textsubscript{7} and weaker lines for VCrO\textsubscript{7}. The band at 1033 cm\textsuperscript{-1} was assigned to V-O stretches in monovanadates and polyvanadates, and the broad 750–1000 cm\textsuperscript{-1} bands were assigned to V-O-V stretches in two-dimensional polyvanadates.\textsuperscript{20,22,54} Crystalline V\textsubscript{2}O\textsubscript{5} gives sharp intense Raman bands at 1002, 708, 535, 490, 410, 305, 289, 203, and 150 cm\textsuperscript{-1}. At low VO\textsubscript{x} surface densities (1.9 V/mm\textsuperscript{2}), the ratio of the 1033 cm\textsuperscript{-1} band intensity (V=O stretch) to that for the 946 cm\textsuperscript{-1} band (V=O-V stretch) is high, indicating that monovanadates predominate on these samples.
Polyvanadates become evident from emerging bands at 700–1000 cm\(^{-1}\) as VO\(_x\) surface density increases from 1.9 to 8.7 V/nm\(^2\). Crystalline V\(_2\)O\(_5\) was detected at high VO\(_x\) surface density (>8 V/nm\(^2\)) from its two bands at 1002 and 708 cm\(^{-1}\), consistent with saturation of polyvanadate monolayers at 7–8 V/nm\(^2\).\(^{57}\) Raman scattering cross sections for bulk V\(_2\)O\(_5\) are 10 times larger than for monovanadates.\(^{58}\) Thus, dispersed VO\(_x\) species remain predominant in 15VAl and 18VAl samples.

Raman spectra for dehydrated 12MoAl and V-coated 12MoAl samples with various VO\(_x\) surface densities (xV12MoAl, x = 3–15; 1.6–9.7 V/nm\(^2\)) are shown in Figure 3. 12MoAl showed bands at 1013 and 842 cm\(^{-1}\), attributed to Mo=O and Mo–O–Mo stretches, respectively.\(^{36,59–61}\) Raman bands for crystalline MoO\(_3\) were not detected on samples prepared using molybdanyl acetylacetonate as the precursor and a surface density of 5.0 Mo/nm\(^2\), corresponding to approximately one monolayer.\(^{52}\) In contrast, MoAl samples prepared with ammonium heptamolybdate showed crystalline MoO\(_3\) bands at surface densities above 4.5 Mo/nm\(^2\).\(^{36,50}\) Only a small unresolved band at 1034 cm\(^{-1}\), assigned to V=O stretches, appeared when VO\(_x\) was deposited on 12MoAl at low surface densities (Figure 3, 3V12MoAl; 1.6 V/nm\(^2\)). Higher VO\(_x\) surface densities led to two new bands at 771 and 239 cm\(^{-1}\), together with a more intense band at 1013 cm\(^{-1}\), which was also present in the spectrum for 12MoAl. The 771 cm\(^{-1}\) band was previously assigned to Mo=O–V stretches in molybdovanadates.\(^{50,51}\) The intensities for the bands at 1013, 771, and 239 cm\(^{-1}\) change to similar extents with increasing VO\(_x\) surface density; thus, they appear to arise from a common V–Mo oxo-structure containing V–O–Mo linkages. A definitive assignment is not possible, but their sharp nature and concurrent appearance with AlMoVO\(_7\) diffraction lines in 10V12MoAl (Figure 1) suggest that they arise from this crystalline phase. The 10V12MoAl sample, which contains an equivalent VO\(_x\) monolayer on Al\(_2\)O\(_3\) pre-coated with a similar equivalent MoO\(_x\) monolayer, showed the most intense bands at 1013, 771, and 239 cm\(^{-1}\) (Figure 3), consistent with intimate mixing between VO\(_x\) and MoO\(_x\) species. Raman bands at 705 and 1002 cm\(^{-1}\) for crystalline V\(_2\)O\(_5\) were detected at VO\(_x\) surface densities of 9.7 V/nm\(^2\) (15V12MoAl).

Raman spectra for 10V\(_x\)MoAl (x = 4–20) samples, which contain an equivalent VO\(_x\) monolayer on Al\(_2\)O\(_3\) supports modified by varying amounts of MoO\(_x\), are shown in Figure 4. Raman spectra for 10V4MoAl (Figure 4) and 10VAl (Figure 2) are similar. Bands at 1013, 771, and 239 cm\(^{-1}\), corresponding to V–Mo–(Al)=O phases, were detected as MoO\(_x\) surface density increased; these bands reached maximum intensities for 10V12MoAl, which contains equivalent monolayers of both VO\(_x\) and MoO\(_x\) components. Diffraction patterns suggest here also that these new bands arise from crystalline AlVMoO\(_7\) structures. Crystalline MoO\(_3\) was detected at surface densities above 6.9 Mo/nm\(^2\). The 1043 cm\(^{-1}\) band for V=O stretching modes in monovanadates and polyvanadates decreased monotonically with
increasing MoO$_x$ surface density. Traces of crystalline V$_2$O$_5$ were detected on 10V8MoAl and 10V16MoAl. The residual coexistence of crystalline V$_2$O$_5$ and MoO$_3$ in 10V16MoAl indicates that V–Mo–O phases form more readily from dispersed MoO$_x$ and VO$_x$ than from crystalline V$_2$O$_5$ and MoO$_3$ at this treatment temperature.

MoO$_x$ species were supported on Al$_2$O$_3$ precoated with an equivalent VO$_x$ monolayer in an effort to explore the effects of deposition sequence on the structure and function of dispersed binary oxides. Figure 5 shows that a mixed V–Mo–O phase is present in 12Mo10VAl and 20Mo10VAl (bands at 1013, 771, and 239 cm$^{-1}$), but its characteristic bands are less intense than for similar compositions prepared via the reverse sequence (Figure 4; 10V12MoAl). Crystalline V$_2$O$_5$ was detected in 4Mo10VAl and 12Mo10VAl, possibly because of the detachment and recrystallization of dispersed VO$_x$ structures during subsequent impregnation with MoO$_x$ precursors. As MoO$_x$ surface densities exceed one equivalent MoO$_x$ monolayer in 20Mo10VAl, intense bands appear at 1000, 823, 680, and 320 cm$^{-1}$, corresponding to crystalline MoO$_3$.

Figure 6 shows Raman spectra for 12CrAl and xV12CrAl (x = 3–15) treated in flowing dry air at 673 K for 1 h. Band arises from symmetric stretches in the O=Cr=O group within chromates, while the 879 and 799 cm$^{-1}$ bands reflect Cr–O–Cr stretches in dichromates and trichromates, respectively. The weak band at 986 cm$^{-1}$ is assigned to CrO$_3$ (bands at 975 and 495 cm$^{-1}$), but crystalline Cr$_2$O$_3$ (with a band at 550 cm$^{-1}$) was not detected in any of the samples.39, 56 Raman bands at 1009, 986, 879, and 799 cm$^{-1}$ weakened upon addition of VO$_x$ to 12CrAl samples and were ultimately replaced by a band at 1037 cm$^{-1}$ assigned to V–O–Cr oligomers. Crystalline V$_2$O$_5$ was not detected, even at the highest VO$_x$ surface density (15V12CrAl; 9.4 V/nm$^2$).

Figure 7 shows Raman spectra for 10VAl and 10V$_x$CrAl (x = 1–15) treated in flowing dry air at 673 K for 1 h. The $\lambda$ band at 986 cm$^{-1}$ is assigned to CrO$_3$ (bands at 975 and 495 cm$^{-1}$), but crystalline Cr$_2$O$_3$ (with a band at 550 cm$^{-1}$) was not detected in any of the samples.39, 56 Raman bands at 1009, 986, 879, and 799 cm$^{-1}$ weakened upon addition of VO$_x$ to 12CrAl samples and were ultimately replaced by a band at 1037 cm$^{-1}$ assigned to V=O stretches and by two broad bands at 940 and 820 cm$^{-1}$. The broad nature of these two latter bands suggests that they arise from well-dispersed structures. Definitive assignment of the band at 940 cm$^{-1}$ is not possible. It appears at a frequency similar to that for orthorhombic CrVO$_4$ (924 cm$^{-1}$), but the absence of corresponding diffraction lines suggests that it exists as disordered and highly dispersed CrVO$_4$ domains, which tend to form at low temperature.68–70 The origin of the 830 cm$^{-1}$ band is unclear; it may reflect the presence of polychromates, polyvanadates, or mixed V–O–Cr oligomers. Crystalline V$_2$O$_5$ was not detected, even at the highest VO$_x$ surface density (15V12CrAl; 9.4 V/nm$^2$).

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weaker, while the 930 cm\(^{-1}\) band became stronger, possibly due to CrVO\(_4\) formation. Only the 820 and 930 cm\(^{-1}\) bands remained at CrO\(_x\) surface densities above 3.7 Cr/nm\(^2\). The replacement of multiple bands for polyvanadates in 10VAl (Figure 2) with two bands at 820 and 930 cm\(^{-1}\) in xV12CrAl\((x = 7-15)\) suggests that VO\(_x\) species formed CrVO\(_4\) species or dispersed more uniformly on CrO\(_x\)-Al\(_2\)O\(_3\) than on pure Al\(_2\)O\(_3\) supports.

Raman spectra for 12MoAl, 10V12MoAl, and 12MoVAl and those for 12CrAl, 10V12CrAl, and 12Cr10VAl are compared in Figure 8a and b. Mixed Mo–O–V structures were detected on both 10V12MoAl and 12Mo10VAl. The spectra for 10V12CrAl and 12Cr10VAl are very similar, suggesting that the binary dispersed oxide structures formed are essentially independent of deposition sequence. Both spectra show a band at 930 cm\(^{-1}\), similar to that observed in CrVO\(_4\) (924 cm\(^{-1}\)).

3.1.2. Reduction of the Catalysts. Figure 9a shows reduction profiles for 10VAl, 12MoAl, 10V12MoAl, 12CrAl, and 10V12CrAl catalysts and (b) Arrhenius plots of the initial rate of H\(_2\) consumption during TPR.

![Figure 8](image1.png)  
**Figure 8.** Raman spectra of (a) 12MoAl, 10V12MoAl, and 12MoVAl and (b) 12CrAl, 10V12CrAl, and 12Cr10VAl.

![Figure 9](image2.png)  
**Figure 9.** (a) TPR profiles of 10VAl, 12MoAl, 10V12MoAl, 12CrAl, and 10V12CrAl catalysts and (b) Arrhenius plots of the initial rate of H\(_2\) consumption during TPR.

Reduction profiles for 12CrAl and 10V12CrAl are shown in Figure 9a; their interpretation is more complex than from Mo–V systems, because of the tendency of CrO\(_x\) structures to autoreduce to various extents during thermal treatments. The peak at 578 K for 12CrAl corresponds to reduction of Cr\(^{6+}\) to Cr\(^{3+}\); Table 4 shows, however, that measured H\(_2\) consumption ratios are smaller than expected for the reduction of all Cr atoms in the sample from Cr\(^{6+}\) to Cr\(^{3+}\), suggesting that only ~60% of Cr cations exist as Cr\(^{6+}\) in 12CrAl.
after thermal treatment in air. This proposal was confirmed by the fraction of the Cr as Cr$^{6+}$ in $x$CrAl ($x = 1$–12) (see Figure A of Supporting Information); in these samples, the fraction of the Cr as Cr$^{6+}$ decreased monotonically from unity to 0.6 as $x$ increased from 1 to 12 (i.e., 0.5–8 Cr/nm$^2$). Oxide supports stabilize surface chromate species in hexavalent form, but Cr atoms in excess of those required for a polychromate monolayer form a three-dimensional structure that reduces to trivalent species to form Cr$_2$O$_3$ during thermal treatment in air.$^{64,72}$–$74$

Our findings indicate that such Cr$^{3+}$ structures start to form at CrO$_x$ surface densities above >2 Cr/nm$^2$.

The 10V12CrAl samples show two overlapping reduction features at 578 and 693 K, which were assigned to CrO$_x$ and VO$_x$ reduction, respectively. The CrO$_x$ reduction peak in 10V12CrAl appears as a small shoulder next to the VO$_x$ reduction peak, even though the number of lattice oxygens associated with VO$_x$ and CrO$_x$ in this sample are similar, indicating that the fraction of the Cr atoms as Cr$^{6+}$ in 10V12CrAl is significantly smaller than that in 12CrAl. In contrast, all V$^{5+}$ reduce to V$^{3+}$ in this sample. These data indicate that the deposition of a nominal monolayer of VO$_x$ on 12CrAl leads to the reaction of most CrO$_x$ species with VO$_x$ to form dispersed CrVO$_4$ during thermal treatment.

### Table 4: Assignments of TPR Results Reported in Figures 9 and 10

<table>
<thead>
<tr>
<th>sample</th>
<th>reduction peak temperature (K)</th>
<th>assignment</th>
<th>$H_2/M$ (M = V, Mo, or Cr) (theoretical values are given in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10VAl</td>
<td>710–745</td>
<td>V$^{5+}$$\rightarrow$V$^{3+}$</td>
<td>0.92 ($H_2/V$ = 1)</td>
</tr>
<tr>
<td>12MoAl</td>
<td>710</td>
<td>Mo$^{6+}$$\rightarrow$Mo$^{4+}$</td>
<td>0.86 ($H_2/Mo$ = 1)</td>
</tr>
<tr>
<td>1053</td>
<td>Mo$^{4+}$$\rightarrow$Mo$^{0}$</td>
<td>2.02 ($H_2/Mo$ = 2)</td>
<td></td>
</tr>
<tr>
<td>12CrAl</td>
<td>578</td>
<td>Cr$^{6+}$$\rightarrow$Cr$^{3+}$</td>
<td>0.91 ($H_2/Cr$ = 1.5)</td>
</tr>
<tr>
<td>10V12MoAl</td>
<td>786</td>
<td>V$^{5+}$$\rightarrow$V$^{3+}$</td>
<td>0.99 ($H_2/(V$ + Mo) = 1)</td>
</tr>
<tr>
<td>1053</td>
<td>Mo$^{6+}$$\rightarrow$Mo$^{4+}$</td>
<td>1.9 ($H_2/Mo$ = 2)</td>
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</tr>
<tr>
<td>12Mo10VAl</td>
<td>760</td>
<td>V$^{5+}$$\rightarrow$V$^{3+}$</td>
<td>0.89 ($H_2/(V$ + Mo) = 1)</td>
</tr>
<tr>
<td>1053</td>
<td>Mo$^{4+}$$\rightarrow$Mo$^{0}$</td>
<td>2.1 ($H_2/Mo$ = 2)</td>
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<tr>
<td>10V12CrAl</td>
<td>572</td>
<td>Cr$^{6+}$$\rightarrow$Cr$^{3+}$</td>
<td>0.12 ($H_2/Cr$ = 1.5)</td>
</tr>
<tr>
<td>693</td>
<td>V$^{5+}$$\rightarrow$V$^{3+}$</td>
<td>1.08 ($H_2/V$ = 1)</td>
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</tr>
<tr>
<td>12Cr10VAl</td>
<td>572</td>
<td>Cr$^{6+}$$\rightarrow$Cr$^{3+}$</td>
<td>0.29 ($H_2/Cr$ = 1.5)</td>
</tr>
<tr>
<td>712</td>
<td>V$^{5+}$$\rightarrow$V$^{3+}$</td>
<td>0.91 ($H_2/V$ = 1)</td>
<td></td>
</tr>
</tbody>
</table>

The 10V12CrAl samples show two overlapping reduction features at 578 and 693 K, which were assigned to CrO$_x$ and VO$_x$ reduction, respectively. The CrO$_x$ reduction peak in 10V12CrAl appears as a small shoulder next to the VO$_x$ reduction peak, even though the number of lattice oxygens associated with VO$_x$ and CrO$_x$ in this sample are similar, indicating that the fraction of the Cr atoms as Cr$^{6+}$ in 10V12CrAl is significantly smaller than that in 12CrAl. In contrast, all V$^{5+}$ reduce to V$^{3+}$ in this sample. These data indicate that the deposition of a nominal monolayer of VO$_x$ on 12CrAl leads to the reaction of most CrO$_x$ species with VO$_x$ to form dispersed CrVO$_4$ during thermal treatment.

![Figure 10](image1.png)

**Figure 10.** Comparison of TPR profiles for (a) 10V12MoAl and 12Mo10VAl and (b) 10V12CrAl and 12Cr10VAl.

![Figure 11](image2.png)

**Figure 11.** UV–visible spectra of 10VAl, 10V12MoAl, and 10V12CrAl treated at 723 K in flowing dry air for 0.5 h.

![Figure 12](image3.png)

**Figure 12.** Weight-based activity of $x$VAl, $x$V12MoAl, and $x$V12CrAl for (a) C$_3$H$_8$ consumption and (b) C$_3$H$_6$ formation.
Reduction profiles for 12Cr10VAl and 10V12CrAl (Figure 10b) show that the CrO\textsubscript{x} reduction peak at 572 K is smaller in the latter sample. Consistent with this, Table 4 shows that the fraction of the Cr atoms present as Cr\textsuperscript{6+} is higher in 12Cr10VAl than in 10V12CrAl; this indicates that 12Cr10VAl contains a smaller fraction of the CrO\textsubscript{x} as CrVO\textsubscript{4} than 10V12CrAl. This may be the reason that the reactivity of 12Cr10VAl is more similar to 12CrAl rather than 10VAl, as we report in the next section. The reduction profiles in Figure 9a indicate that VO\textsubscript{x} species reduce faster in 10V12CrAl than in 10VAl, while the MoO\textsubscript{x} layer in 10V12MoAl leads to slower VO\textsubscript{x} reduction than in 10VAl. Arrhenius plots of the initial H\textsubscript{2} consumption rates obtained during the early stages of the stoichiometric reduction of these oxides in H\textsubscript{2} (<15% reduction) are shown in Figure 9b. The initial H\textsubscript{2} consumption rates in 10V12CrAl are higher than in 10VAl at all temperatures, while rates in 10V12MoAl are lower than in VAl. We expect and indeed find significant catalytic consequences of these reducibility trends for oxidative dehydrogenation reactions, as we discuss below.

3.1.3. UV–Visible Characterization. UV–visible spectra are shown in Figure 11 for 10VAl, 10V12MoAl, and 10V12CrAl. The spectra for 10VAl and 10V12MoAl are similar and show an absorption feature at 3.1 eV, while 10V12CrAl shows more intense absorption features, including two at 1.8 and 2.5 eV, corresponding to d–d transitions in Cr\textsuperscript{3+} centers and charge transfer in polychromates,\textsuperscript{39,64} without detectable spectral contributions from V\textsuperscript{5+}.

UV–visible edge energies for 10VAl and 10V12MoAl samples are 2.25 and 2.40 eV, respectively. A previous study\textsuperscript{23} reported that ODH turnover rates increased with decreasing
absorption edge energy; thus, 10VAl would be expected to show lower ODH rates than 10V12MoAl, as found experimentally and reported below. The 10V12CrAl sample does not show an absorption edge, apparently because it occurs below 1.5 eV.

In summary, Raman, reduction, and UV-visible data indicate that polyvanadate structures predominate in VAl samples. Mixed metal oxides form when MoO$_3$ is placed below or above VO$_x$, which leads to less reducible oxides and to higher absorption edge energies than in VAl. Raman and reduction results also show that most CrO$_x$ species react with VO$_x$ to form CrVO$_4$ when VO$_x$ is deposited over a nominal CrO$_x$ monolayer on Al$_2$O$_3$, but that some CrO$_x$ remains unreacted when it is deposited over a nominal monolayer of VO$_x$ on Al$_2$O$_3$.

**3.2. Oxidative Dehydrogenation Rates and Selectivities.** Rates normalized by catalyst mass are shown in Figure 12 for C$_3$H$_8$ conversion and C$_3$H$_6$ formation on VAl, V12MoAl, and V12CrAl as a function of VO$_x$ surface density. As reported previously,22 ODH rates on xVAl increase with increasing VO$_x$ surface density and reach constant values at ~7 V/nm$^2$. These trends reflect the higher VO$_x$ content and specific reactivity with increasing surface density, as more reactive polyvanadates replace less active and reducible monovanadate structures.23 VO$_x$ surface density effects on primary ODH rates (per V-atom) and selectivities and on rate constant ratios are shown in Figure 13 for xVAl, xV12MoAl, and xV12CrAl. For xV12MoAl and xV12CrAl, catalytic contributions from the part of the surface not covered by VO$_x$ species were subtracted from measured rates and residual VO$_x$ contributions were normalized by the V-atoms in each sample. This procedure assumes that the fraction of the support covered by VO$_x$ is proportional to VO$_x$ surface density up to 7 V/nm$^2$ and that exposed Mo- and Cr-coated surfaces catalyze reactions with rates similar to those on 12MoAl and 12CrAl samples.

Primary rates for propane conversion and propene synthesis increased with increasing VO$_x$ surface density and reached maximum values at ~7 V/nm$^2$ on xVAl (Figure 13a and b), corresponding to an equivalent polyvanadate monolayer, as reported previously.22 This trend reflects the higher reactivity of oligomeric VO$_x$ species relative to VO$_x$ monomers as the VO$_x$ coverage increases and is consistent with a concurrent decrease in absorption-edge energies and an increase in the rate of stoichiometric VO$_x$ reduction with H$_2$.

Figure 13d and e shows that $k_2/k_1$ ratios increase and $k_3/k_1$ ratios decrease with increasing VO$_x$ surface density on xVAl. These trends reflect the increasing propensity for propane to undergo combustion as the surface of alumina is covered by vanadia, and the tendency for propene to react less readily with increasing vanadia coverage. The latter trend is a consequence of the reduction in exposed alumina surface, on which are present Brønsted acid sites. A decrease in the exposure of such sites to the gas phase lowers the ease of adsorption of the newly formed olefin.

Effects of VO$_x$ surface density on primary ODH rates (per V-atom) are also observed on xV12MoAl and xV12CrAl. At low VO$_x$ surface densities (<3 V/nm$^2$), rates on xV12MoAl and xV12CrAl are similar and higher than on xVAl. At higher VO$_x$ surface densities, rates on xV12MoAl become lower than on xVAl. This behavior appears to reflect the mixing of V and Mo species, leading to the replacement of V=O−V structures with less reactive V=O−Mo structures. Below 3 V/nm$^2$, monovanadates prevail on both Al$_2$O$_3$ and 12MoAl surfaces (Figure 3) and V=O−Al species in xVAl are thus replaced, at least in part, by V=O−Mo, leading to greater reducibility and ODH reaction rates. Above 3 V/nm$^2$, polyvanadates form on xVAl, while mixed oxides form on xV12MoAl, leading to a net replacement of more reactive V=O−V species with less reactive V=O−Mo structures. Thus, active catalytic structures in polyvanadates are rendered less active by dilution with Mo=O linkages. This interpretation is consistent with the lower reduction rates and higher reduction peak temperature in 10V12MoAl than on 10VAl for samples containing predominantly polyvanadate and oligomeric Mo=O−V structures (Figure 9).

These trends of mixed VO$_x$ and MoO$_x$ structures differ from those reported previously,20 that study reported that 10V12MoAl shows higher ODH rates (per V-atom) than 10VAl. These differences reflect the use of different VO$_x$ precursors used to prepare 10VAl (ammonium metavanadate) and 10V12MoAl (vanadyl isopropoxide) in the previous study.20 Figure 14 shows Raman spectra for 12MoAl, 10.5VAl, and 10V12MoAl reported previously and for identical compositions prepared by the methods used here (see Experimental Section). The use of ammonium heptamolydate and ammonium metavanadate as precursors led to low MoO$_3$ and VO$_x$ dispersions on alumina, as evidenced by the appearance of bands for MoO$_3$ and V$_2$O$_5$ in these samples.20 The bands for oligomeric MoO$_3$ and VO$_x$ are also less intense than those observed in the samples prepared for the present study. On the other hand, the samples of 10V12MoAl prepared previously exhibit a Raman spectrum.
very similar to that reported here, with clear evidence for Mo–O–V structures (1013, 771, and 239 cm\(^{-1}\) bands). Thus, the higher ODH rates (per V-atom) reported earlier for 10V12MoAl relative to 10VAl are due predominantly to differences in synthetic methods. The results and conclusions in the present study are consistent with those of Banares and Khatib,\(^{51}\) who found no synergistic effects in VO\(_x\)-MoO\(_x\)/Al\(_2\)O\(_3\) samples prepared by coimpregnation of V and Mo precursors.

Figure 13d shows that \(k_2 / k_1\) values are much lower on xV12MoAl than on xVAl, especially for VO\(_x\) surface densities above 5 V/nm\(^2\). Values of \(k_2 / k_1\) are lower on xV12MoAl than on xVAl for VO\(_x\) surface densities below 4 V/nm\(^2\), but these trends are reversed at higher VO\(_x\) surface densities. At low surface densities, these effects reflect the coverage of MoO\(_x\) species by more selective VO\(_x\) domains, as shown by the higher value of \(k_2 / k_1\) measured for a MoO\(_x\) monolayer on Al\(_2\)O\(_3\) than for a similar VO\(_x\) monolayer (Figure 13e). Thus, partial coverage of 12MoAl surfaces by VO\(_x\) would lead to the observed initial decrease in \(k_2 / k_1\) values with increasing surface density in xV12MoAl samples. These effects are ultimately reversed as mixing of the VO\(_x\) and MoO\(_x\) structures occurs with increasing VO\(_x\) surface density, a process that leads to higher \(k_2 / k_1\) ratios.

Primary ODH rates (per V-atom) on xV12CrAl exceed those on xVAl, even after subtracting contributions from exposed 12CrAl surfaces, at all VO\(_x\) surface densities (Figure 13). Both Raman spectra and reduction profiles for xV12CrAl indicate that VO\(_x\) increases the fraction of CrO\(_x\) that forms CrVO\(_4\).
Therefore, the higher specific ODH rates per V-atom of xV12CrAl relative to xVAl are attributed to the formation of V-O-Cr structures, which replace V-O-Al sites at low VOx surface densities. The value of \( k_2/k_1 \) on 12CrAl (1.1) is higher than on 10VAl (0.2) and decreases with increasing VOx surface density up to 3 V/nm² (Figure 13d). Above this V-content, \( k_2/k_1 \) increases with VOx surface density as in xVAl samples. Thus, the blocking of CrOx oligomers, with high propane combustion reactivity, by VOx reduces their contribution to combustion pathways, presumably because an increasing fraction of exposed surfaces consist of VOx or VCrOx domains. In contrast, values of \( k_3/k_1 \) are very low on 12CrAl, and VOx deposition leads to higher values at low VOx surface densities, but ultimately to a decrease similar to that observed on xVAl as VCrOx species form with increasing surface density.

The interpretations of the effects of MoOx and CrOx underlayers on the structure and catalytic properties of VOx domains presented above are consistent with the data in Figure 15 for samples in which an equivalent VOx monolayer is deposited onto an Al₂O₃ surface partly or fully covered by MoOx or CrOx. Partial MoOx coverages decreased ODH rate (per V-atom) because Mo-O-V bonds are less reactive than the V-O-V bonds prevalent in 10VAl at these VOx surface densities. With increasing MoOx surface density, \( k_2/k_1 \) decreases and \( k_3/k_1 \) increases. This is consistent with the lower \( k_2/k_1 \) values and higher \( k_3/k_1 \) ratios on MoOx than VOx domains (Figure 13).

Partial coverage of Al₂O₃ by CrOx leads to effects opposite to those observed for equivalent MoOx coverages. ODH rates (per V-atom) increased monotonically, while \( k_2/k_1 \) increased and \( k_3/k_1 \) decreased, with increasing CrOx surface density.

Temperature effects on propane consumption, propene selectivity, and \( k_2/k_1 \) and \( k_3/k_1 \) ratios are shown in Figure 16 for similar VOx monolayers in 10VAl, 10V12MoAl, and 10V12CrAl. At all temperatures, the rate of propane conversion is higher for VOx dispersed on 12CrAl than on Al₂O₃, while VOx deposited onto 12MoAl leads to lower rates than on Al₂O₃. Propene selectivities are highest on 10V12MoAl and lowest on 10V12CrAl, with 10VAl giving intermediate values. On all three catalysts, propane consumption rates increased and propene selectivities decreased with increasing temperature; the latter reflects the observed increase in \( k_2/k_1 \) with temperature, which arises from slightly higher activation energy for combustion than for dehydrogenation of propane. In contrast, \( k_3/k_1 \) decreases markedly with increasing temperature, as expected from the lower activation energies involved in cleaving allylic C-H groups in propene as compared to those required for activation of stronger methylene C-H bonds in propane.19 Temperature effects on \( k_2/k_1 \) are stronger on 10V12MoAl than on 10VAl or 10V12CrAl samples, but temperature effects on \( k_3/k_1 \) are more marked on 10V12CrAl than on 10VAl or 10V12MoAl.

The extent of mixing between an equivalent VOx monolayer and supports coated with MoOx or CrOx monolayers was probed...
by reversing the order of layer deposition. The effects of deposition sequence on dehydrogenation rates and on \( k_2/k_1 \) and \( k_3/k_1 \) ratios are shown as a function of temperature in Figure 17. Dehydrogenation rates (per mass) are 1.3 times higher at 673 K when MoO\(_x\) was deposited first. Below 635 K, \( k_2/k_1 \) is lower on 10V12MoAl than on 12Mo10VAl, but it becomes larger above 635 K, because of the stronger effects of temperature on \( k_2/k_1 \) on the 10V12MoAl sample. Values of \( k_3/k_1 \) are very similar on 10V12MoAl and 12Mo10VAl, although the value of \( k_3/k_1 \) for 10V12MoAl decreases somewhat more rapidly with increasing temperature. These effects of deposition sequence reflect significant but incomplete mixing between VO\(_x\) and MoO\(_x\) monolayers. Raman spectra for 10V12MoAl and 12Mo10VAl showed bands for mixed Mo–O–V structures (Figure 8), especially when MoO\(_x\) is deposited first (10V12MoAl), but their reduction profiles are very similar (Figure 10). These data, taken together with the observed catalytic consequences of deposition sequence (Figure 17), indicate that significant mixing occurs during deposition or subsequent thermal treatment in VO\(_x\)–MoO\(_x\) binary dispersed oxide samples. The small remaining catalytic differences between 10V12MoAl and 12Mo10VAl reflect the presence of small amounts of VO\(_x\) at 10V12MoAl surfaces and small amounts of MoO\(_x\) at 12Mo10VAl surfaces.

For binary dispersed oxide samples containing equivalent monolayers of VO\(_x\) and CrO\(_x\), the rate of propane ODH (per mass) is 1.5 times higher when CrO\(_x\) is deposited first (10V12CrAl) instead of VO\(_x\) (12Cr10VAl). The effects of temperature on \( k_2/k_1 \) are strongly influenced by the sequence of deposition; \( k_2/k_1 \) increases with temperature on 10V12CrAl, as was also found on 10VAl, but shows the opposite trend on 12Cr10VAl, as was also observed on 12CrAl. These effects of deposition sequence suggest that the surfaces of these dispersed binary oxides retain some of the properties of the oxide deposited last, even though most VO\(_x\) and CrO\(_x\) species interact to form mixed oxides, for example, CrVO\(_4\). Values of \( k_3/k_1 \) are...
higher on 10V12CrAl than on 12Cr10VAl and decrease with temperature on both samples. These data also suggest the predominant exposure of the oxide deposited last, because $k_3/k_1$ values are lower on 12CrAl than on 10VAl (Figure 13), and both samples show a decrease in $k_3/k_1$ ratios with increasing temperature (10VAl in Figure 16, temperature effects on 12CrAl not shown). These catalytic consequences of deposition order are much stronger than any structural changes detectable in their Raman spectra (Figure 8), from which it is not possible to assess the extent of mixing in 10V12CrAl and 12Cr10VAl. Reduction profiles for these two samples, however, provide definitive evidence for mixing of VO and CrO components in these samples. The reduction peak at 572 K (Figure 9), attributable to reduction of exposed CrO$_x$ (Figure 8), is more pronounced in 12Cr10VAl than in 10V12CrAl, suggesting that CrO$_x$ is preferentially exposed at the surface of 12Cr10VAl, consistent with the observed catalytic consequences of the deposition sequence.

4. Conclusions

The deposition of vanadia on alumina covered by an equivalent monolayer of molybdena produces well-dispersed VO$_x$ domains at low V surface densities and results in the formation of a mixed metal oxide (AlMoVO$_4$) at higher V surface densities. This mixed metal oxide is less readily reducible than the polyanvate species that form on the surface of alumina at an equivalent monolayer coverage. For V surface densities below 3 V/nm$^2$, the specific activity of VMoAl and VMoCrAl of alumina at an equivalent monolayer coverage. For V surface densities. This mixed metal oxide is less readily reduced to VO$_x$ and CrO$_x$ components in these samples. The reduction peak at 572 K (Figure 9), attributable to reduction of exposed CrO$_x$ (Figure 8), is more pronounced in 12Cr10VAl than in 10V12CrAl, suggesting that CrO$_x$ is preferentially exposed at the surface of 12Cr10VAl, consistent with the observed catalytic consequences of the deposition sequence.

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Supporting Information Available: Figures of the percent-age of Cr as Cr$^{3+}$ in xCrAl, xV12CrAl, and 12Cr10VAl catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes
