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Molecular structure and reactivity of titania-supported transition metal oxide catalysts synthesized by equilibrium deposition filtration for the oxidative dehydrogenation of ethane

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ABSTRACT

The molecular structure and catalytic performance of $(\text{MoO}_x)_n/\text{TiO}_2$, $(\text{WO}_x)_n/\text{TiO}_2$ and $(\text{VO}_x)_n/\text{TiO}_2$ catalysts (synthesized by the equilibrium–deposition–filtration/EDF method) for oxidative dehydrogenation (ODH) of ethane were studied by *in situ* Raman spectroscopy at 430 °C and catalytic measurements in the temperature range of 420–480 °C. The extent of association within the deposited oxometallic phase followed the sequence $(\text{VO}_x)_n/\text{TiO}_2 \gg (\text{MoO}_x)_n/\text{TiO}_2 > (\text{WO}_x)_n/\text{TiO}_2$; a concurrent trend in reduction susceptibility was evidenced by exploiting the relative normalized Raman band intensities while monitoring the response of the vibrational properties of the catalytic samples under reactive ($\text{C}_2\text{H}_6/\text{O}_2/\text{He}$) and reducing ($\text{C}_2\text{H}_6/\text{He}$) conditions by *in situ* Raman spectroscopy. The catalyst reactivity tracks the corresponding trend in reduction susceptibility as evidenced by the *in situ* Raman spectra. Selective reaction pathways are favored at high coverage whilst combustion routes are activated at low coverages due to the involvement of carrier lattice oxygen sites. The observed apparent reaction rates and activation energies are discussed in relation to various structural and reactivity aspects.

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1. Introduction

The catalytic dehydrogenation of light alkanes by selective oxidation is an attractive route for the synthesis of C_2 – C_4 olefins [1–10]. In contrast to the direct dehydrogenation (DH) [6], the presence of O_2 as an oxidant (ODH) [4,5,7–10] contributes to an exo-thermicity that helps to achieve a control over the carbon deposition problem, albeit to the expense of the performance in selectivity grounds. Therefore, the achievement of high selectivities at significant conversions is of utmost importance and

remains a formidable challenge in the design of efficient catalysts for the ODH of light alkanes.

Oxides of transition metals (e.g., V, Mo, W, etc.) in the form of a deposited oxometallic phase on a typical oxidic support (e.g., Al_2O_3 , TiO_2 , etc.) constitute a well-established class of catalytic materials that have been examined for the ODH catalytic reaction [3–5,8,9,11,12–17]. The choice of a particular transition metal oxide (as the active phase) greatly affects the catalyst performance. For example, V_2O_5 -based catalysts are by far superior to their respective MoO_3 -based counterparts for the ODH of light alkanes [17,18]. The efficient activation of the C–H alkane bond is directly related to *inter alia*: (a) the speciation of the oxometallic species in the deposited phase; (b) the local structure at the molecular level; (c) the active phase coverage; (d) the nature of the support; (e) the applied synthesis route.

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Most commonly, the studied catalysts are synthesized by wet impregnation involving a contact of the support grains with a solution containing the oxometallic precursor species at a specified pH and concentration and removal of the solvent by evaporation. Typically, such a step is followed by drying and calcination. However, during the evaporation of the solvent, drastic changes occur in the concentration and pH of the impregnating solution, thereby greatly affecting the speciation of the oxometallic solute species (resulting also in massive precipitation and formation of overlayers).

The application of the *equilibrium deposition filtration* (EDF) synthesis method (also called equilibrium adsorption method) gives rise to catalyst materials with high dispersion of the deposited species [19]. By applying this technique, certain physicochemical properties can be tailored to a significant extent and thus a suitable catalytic behavior for a given reaction may be obtained through a molecular-level-understanding of the processes taking place at each preparation step. For example, the deposition step takes place at equilibrium with precise control of the deposition pH and the solid–liquid separation takes place by filtration leading to the removal of the non-adsorbed oxometallic precursors with the filtrate, thereby resulting in a high dispersion of oxometallic species on the support. To this end, we have synthesized three series of titania-supported transition metal oxide catalysts [(MoO_x)_n/TiO₂, (WO_x)_n/TiO₂ and (VO_x)_n/TiO₂] and tested them for the ODH of ethane. The catalyst synthesis was done by applying the EDF method in a wide range of deposition pH 9.5–4 and solution concentrations of Mo(VI), W(VI) and V(V) lying on the plateau of the respective adsorption isotherms of Mo(VI), W(VI) and V(V) on TiO₂ [20–22]. *In situ* Raman spectra were recorded at 430 °C under O₂(g) and the response of the catalyst molecular structure was examined by applying reaction conditions (C₂H₆/O₂/He) and reducing conditions (C₂H₆/He). Catalytic measurements were undertaken in the temperature range of 420–480 °C at various residence times. The data are used to discuss structure/activity–selectivity relationships for the ODH of ethane.

2. Experimental

2.1. Synthesis and textural characterization of catalyst samples

The catalyst samples were prepared by the Equilibrium Deposition Filtration (EDF) method. The support material used was industrial titania (Degussa P25, 80% anatase–20% rutile) with a surface composition of 90% anatase and 10% rutile [23,24]. The precursors used for preparing the impregnation solutions were (NH₄)₆Mo₇O₂₄·4H₂O, (NH₄)₁₀W₁₂O₄₁·5H₂O and NH₄VO₃. The ionic strength of the solutions was adjusted with 0.1 M NH₄NO₃. For each synthesis, 3.5 g of titania were added to 175 mL of the respective solution in a 25°C-operated thermostatted double-wall pyrex vessel equipped with a magnetic stirrer and a Perspex lid with appropriate fittings for electrodes and N₂ admission (necessary to prevent CO₂ from interfering with the solution pH). The samples were prepared at different pH (in the range 9.5–4, automatically controlled)

and initial concentrations lying on the plateau of the adsorption isotherms of Mo(VI), W(VI) and V(V) [20–22]. The samples were collected by filtration, following a 24-h equilibration, dried at 110 °C for 4 h and then calcined in air in a muffle furnace at 450 °C for 5 h. The calcined samples are denoted as xMTi, where x denotes the surface density (M/nm²) and M denotes the particular transition metal (M = Mo, W, V). The catalyst loading (% wt M) was found by determining spectrophotometrically the initial and equilibrium concentrations of Mo(VI), W(VI) or V(V) in the impregnation solutions [25]. The surface density (M/nm²) was calculated for each sample by combining the % wt M loading with the corresponding BET specific surface area (S_{BET}).

The specific surface area was measured by N₂ adsorption (following a 2 h evacuation) and standard multipoint BET methods in a Micromeritics Gemini II 2370 analyser. A Philips PW 1830 diffractometer with Cu Kα radiation was used to obtain the X-ray diffraction patterns of the studied catalysts and the only crystalline phase detected was anatase.

Table 1 compiles important synthesis parameters and characteristics of the catalyst samples.

2.2. *In situ* Raman spectroscopy under oxidizing (O₂), ODH reaction and reducing (C₂H₆/He) conditions

A homemade Raman cell (previously described in e.g., [10,26]) was used to record the *in situ* Raman spectra of the catalysts. A detailed description of the apparatus and of the procedures used to record *in situ* Raman spectra from catalyst materials can be found in previous articles [10,26]. Raman spectra were excited using the 488.0 nm line of a Spectra Physics Stabilite 2017 Ar⁺ ion laser. In order to reduce sample irradiance, the incident laser light (adjusted at a 40 mW power level) was slightly defocused.

In situ Raman spectra were obtained for the studied catalysts under flowing (15 cm³ min⁻¹) O₂ gas (99.999%) at 430 °C following a 1 h treatment. Subsequently, for monitoring the response of the catalysts' molecular structure to changes in the reactor gas atmosphere, each sample was subjected to a 20 cm³ min⁻¹ flow of 5.6% C₂H₆/5.6% O₂/He reaction mixture for 1 h and thereby the *in situ* Raman spectrum was recorded under ethane ODH reaction conditions. Finally, each catalyst was reoxidized under flowing O₂ for 1 h and was exposed to a 20 cm³ min⁻¹ flow of 11.2%

Table 1
Synthesis parameters and properties of the MO_x/TiO₂ (M = Mo, W, and V) catalysts.

Catalyst	pH/initial M concentration (M)	Loading, (wt% M)	S _{BET} (m ² /g)	Surface density (M/nm ²)
0.3MoTi	9/10 ⁻²	0.26	53.7	0.3
2.6MoTi	6/1.5 × 10 ⁻²	2.21	53.5	2.6
3.8MoTi	4/2.5 × 10 ⁻²	3.18	51.8	3.8
1.7WTi	9/5 × 10 ⁻³	2.77	52.2	1.7
1.9WTi	7/4.2 × 10 ⁻³	3.03	52.7	1.9
3.8WTi	5/2 × 10 ⁻²	5.89	51.5	3.8
1.9VTi	9.5/6 × 10 ⁻³	0.84	51.7	1.9
2.8VTi	7/5 × 10 ⁻³	1.22	51.7	2.8
4.0VTi	5/2 × 10 ⁻²	1.69	50.6	4.0

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