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Influence of vanadate structure and support identity on catalytic activity in the oxidative cleavage of methyl ketones

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ABSTRACT

Oxidative ketone scissions are an interesting class of reactions; they yield aldehyde and carboxylic acids as products, and they proceed over reducible oxides in the presence of molecular oxygen. This chemistry can be leveraged in the production of bio-based maleic anhydride (MA) from levulinic acid (LA) over supported vanadium oxides. Here, we probe the role of active site structure and support identity in dictating the rate of ketone oxidation. Specifically, we have prepared supported vanadium oxides in a range of loadings on SiO_2, γ-Al_2O_3, TiO_2 and CeO_2, and we have quantified their intrinsic activity in the oxidative cleavage of 2-pentanone. FT-Raman spectroscopy and temperature programmed surface oxidation (TPSO) of adsorbed methanol were employed to probe vanadium speciation and oxidation site densities. Our analysis suggests that the intrinsic activity of supported vanadates is sensitive to both vanadium oxide structure and support identity.

1. Introduction

Lignocellulosic biomass is abundant, carbon-based, and renewable; as such, it is often touted as a sustainable alternative to petroleum. That said, biomass is largely comprised of carbohydrates and lignin, which are heavily oxygenated relative to fossil resources [1–5]. This creates the classic challenge of biorefining: most large-market, petroleum-based commodities (e.g., fuels) are composed of carbon and hydrogen, and matching their properties from biomass requires extensive oxygen removal [6]. More often than not, deep deoxygenation is costly relative to conventional oil refining, which makes it difficult for biomass to compete as a fuel precursor alongside inexpensive crude. To foster development of bio-based technologies in the current landscape, it is essential to identify scenarios where biomass might offer a competitive advantage.

Within a refinery or petrochemical facility, *introducing* chemical functionality to inert alkanes is challenging and expensive. One may, for example, point to the energy demand of aromatic production (naptha reforming) or the difficult selectivity control during partial hydrocarbon oxidation as cost drivers in the production of chemical intermediates [7,8]. In certain cases, it may be advantageous to initiate production of specialty or commodity chemicals by leveraging the inherent reactivity of biomass [9]. Indeed, with the challenges in commercial development of biofuels increasingly apparent, several bio-based strategies aimed at the production of alkenes, dienes, aromatics, and oxygenates have recently come to the forefront [10–14]. Along these lines, we have reported a catalytic pathway for the production of bio-based maleic anhydride (MA), which is based on the oxidative cleavage of the ketone moiety in levulinic acid (LA) over supported vanadium oxides (Scheme 1). The process begins with a sugar derivative (LA), and it offers relatively mild processing and good selectivity compared to conventional butane oxidation [15]. The present article is focused on understanding the role of vanadium oxide structure and support identity in dictating reactivity during ketone oxidation.

Over reducible oxides, oxidative chemistries frequently proceed through a Mars-van-Krevelen mechanism, wherein atomic oxygen is transferred to adsorbed species by concurrent reduction of lattice heteroatoms. This forms reaction products, which desorb to expose an oxygen vacancy. Molecular oxygen then facilitates re-oxidation of the lattice to complete the catalytic cycle [16,17]. Because lattice oxygen plays such a critical role in Mars-van-Krevelen mechanisms, rates of heterogeneously-catalyzed oxidations are often sensitive to changes in the nature of the oxygen-

Abbreviations: MA, maleic anhydride; LA, levulinic acid; TPSO, temperature programmed surface oxidation; FWHM, full width at half maximum; STY, site time yield.

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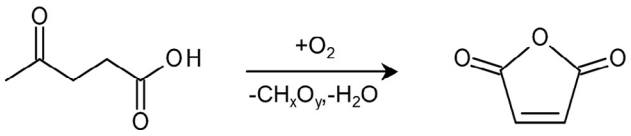

Scheme 1. The oxidation of levulinic acid (4-oxopentanoic acid) yields maleic anhydride. Transforming levulinic acid into maleic anhydride requires oxidative scission of levulinic acid's C_4—C_5 bond. This is a specific example of a generic ketone oxidation.

heteroatom bonds that comprise the active site [18–20]; however, there have been few prior investigations aimed at developing the structure-function relations that govern oxidative scission of ketones; accordingly, we take steps to do so here.

At vanadium oxide surfaces, oxygen atoms can be found in one of three bonding environments: vanadyl oxygens (V═O), vanadium-oxygen-vanadium bonds (V—O—V), and vanadium-oxygen-support bonds (V—O—M, where M is the heteroatom cation in the solid oxide support) [21,22]. The oxygen distribution depends on the local structure adopted by vanadium oxides, of which one can identify three broad categories: isolated, tetrahedral vanadate monomers; oligomeric, surface vanadates that extend in one or two dimensions; and bulk, three-dimensional crystallites (e.g., V_2O_5) [23]. The vanadium oxide distribution is sensitive to the nature of the metal oxide support, the vanadium loading, the vanadium precursor, and the synthetic methodology [24–26]. As the character of the lattice oxygen population changes with the identity of the vanadium phase, so may catalytic reactivity. Further, it is clear that changing the identity of the support cation, M, will perturb the electronic structure of the V—O—M bond, which can make its reduction more or less facile. If reduction or re-oxidation of the V—O—M vanadium is kinetically significant, this perturbation will directly impact oxidation kinetics [25]. In order to probe how intrinsic rates of ketone oxidation respond to changes in vanadate structure and support cation identity, we have prepared twenty catalysts by depositing vanadium at five different fractions of the theoretical monolayer coverage (0.0, 0.1, 0.5, 1.0 and 1.5) onto four oxide supports of varying cation reducibility (SiO_2, γ-Al_2O_3, TiO_2 and CeO_2). Physical and chemical properties of each catalyst were determined by FT-Raman spectroscopy, N_2 physisorption, and temperature-programmed surface oxidation (TPSO) of methanol. In order to build connections between active site structure and catalytic function, we have additionally quantified the activity of each catalyst during oxidation of 2-pentanone, which is a suitable probe reaction for investigating fundamental aspects of oxidative ketone scission.

2. Experimental

2.1. Reagents

Cerium nitrate hexahydrate (Acros Organics, 99.5%), γ-alumina (Strem Chemicals, 95%), titanium dioxide (Acros Organics, Aeroxide® P25), amorphous silica (Sigma-Aldrich, Davisil Grade 633), ammonium metavanadate (Sigma-Aldrich, ≥99.5%) and oxalic acid (Acros Organics, 98%) were used in catalyst synthesis. Vanadium pentoxide (Acros Organics, 98+%) was used as supplied. 2-pentanone (Acros Organics, 99%) was used as a probe molecule. Formaldehyde (Sigma-Aldrich, 37 wt% in H_2O, 10–15% methanol as stabilizer), dimethyl ether (Aldrich Chemistry, ≥99%), acetaldehyde (Sigma-Aldrich, ≥99.5%), acetic acid (Acros Organics, 99.8%), propionaldehyde (Acros Organics, 99+%), propionic acid (Acros Organics, 99%), n-butyric acid (Acros Organics, 99+%), CO (Airgas, 1%, 1% Ar, balance He) and CO_2 (Airgas, 1%, 1% Ar, balance He) were used for calibration of analytical instruments. Methanol (Fisher, Optima 99.9%) was employed for TPSO experiments. Water was purified in house by sequential reverse osmosis, UV oxidation, and double ion exchange to >18.2 MΩ cm resistivity (Spectrapure). He (Airgas, Ultra High Purity) and O_2 (Airgas, Ultra High Purity) were used as diluent and oxidant during reactor operation. Air (Airgas, Ultra Zero Grade) was used for ex-situ calcination of all catalyst samples.

2.2. Catalyst synthesis

Cerium oxide was synthesized by calcination of cerium nitrate hexahydrate in static air at 823 K (5 K min^{-1}, 4 h) [27]. $CeVO_4$ samples were synthesized using an established co-precipitation method [28]. Specifically, an alkaline (NaOH) solution of ammonium metavanadate was reduced by sodium borohydride and subsequently reacted with cerium nitrate to precipitate $CeVO_4$. Vanadium oxides were supported on SiO_2, γ-Al_2O_3, TiO_2, and CeO_2. Vanadium mass loadings were varied on each support to achieve fractions (0.0–1.5) of the theoretical monolayer coverage of VO_x units for that support.

Supported vanadium oxides were prepared by incipient wetness impregnation of ammonium metavanadate dissolved in aqueous oxalic acid. The molar ratio of ammonium metavanadate to oxalic acid was 2:1, and the molar concentration of ammonium metavanadate was varied as necessary to achieve desired vanadium loadings [25,29,30]. Resultant solids were dried at 338 K, crushed to break aggregates, calcined under flowing air at 723 K (60 sccm, 3 K min^{-1}, 4 h), crushed into fine particles, and graded through standard mesh sieves. Treating samples at 723 K in air is sufficient to decompose precursor salts, resulting in deposition of vanadium (+5) oxides on the support surface [31,32]. All characterization and reaction experiments were performed using catalyst particles in the 45–90 μm range. In this manuscript, we refer to quantities defined in Eqs. (1)–(3), which specify vanadium loadings in several dimensions.

$$V_A = \frac{N_V \cdot N_A}{m_S \cdot SA_S} \tag{1}$$

$$V_M = \frac{N_V}{N_V \cdot MW_V + m_S} \tag{2}$$

$$V_W = V_M \cdot MW_V \cdot 100 \tag{3}$$

In these equations, V_A is the areal density of atomic vanadium (V nm^{-2}); V_M is the molar loading of vanadium per unit mass of catalyst (μmol V g^{-1}); V_W is the mass percentage of vanadium in a given catalyst; N_V is the total moles of vanadium in a given catalyst preparation; N_A is Avogadro's number; m_S is the mass of support used in a given catalyst synthesis; SA_S is the support surface area per unit mass determined by N_2 physisorption; and MW_V is the atomic mass of vanadium.

2.3. Surface area and pore size measurements

Surface areas and average pore sizes for each catalyst and support were determined by N_2 physisorption at 77 K (Micromeritics, ASAP 2020). Prior to N_2 dosing, samples were outgassed under vacuum for 4 h at 523 K. Total surface areas were determined by BET analysis. Average pore diameters were determined from BJH analysis of the desorption branch of N_2 uptake isotherms [33,34].

2.4. Raman spectroscopy

Raman spectra were acquired using a Bruker FRA 106 FT-Raman spectrometer equipped with an Nd:YAG laser emitting at 1064 nm. Prior to spectral acquisition, samples were dehydrated ex situ in a