# Catalysis Science & Technology

# PAPER



Cite this: DOI: 10.1039/d0cy01732a

# Tuning selectivity in nickel oxide-catalyzed oxidative dehydrogenation of ethane through control over non-stoichiometric oxygen density\*

Xiaohui Zhao, Mariano D. Susman, Jeffrey D. Rimer  $^{igodot}$  and Praveen Bollini  $^{igodot}$  \*

Despite bulk metal oxide non-stoichiometry often being recognized as a key determinant of catalytic performance, clarifying its catalytic function has remained elusive due in part to the highly complex nature of many catalyst surfaces. In this study, we demonstrate that the non-stoichiometric oxygen (NSO) density for thermally stable nickel oxide cubes can be manipulated without measurable changes in degree of crystallinity, particle size, and morphology. UV-vis spectroscopy, temperature programmed desorption, and H<sub>2</sub>-temperature programmed reduction analyses all evidence monotonic decreases in NSO density upon thermal treatment; crucially, these decreases persist upon exposure to ethane and oxygen under oxidative dehydrogenation of ethane (ODHE) reaction conditions. Such control over NSO density under reaction conditions is used to tune ODHE ethene selectivity; independent of reaction conditions, at isoconversion, ethene selectivity tracks gualitatively with NSO density. These trends in selectivity, however, do not extend to conditions resulting in higher fractional hydroxyl coverages, for example, in the presence of water cofeeds, where primary ODHE selectivities vary only at the highest treatment temperature used in our study. Overall, this study points to (i) the need for well-defined oxide materials that enable (ideally) the exclusive variation of a single physicochemical property, (ii) the importance of using multiple characterization techniques for guantifying various properties, and (iii) the sensitivity of selectivity trends to surface coverages of reaction intermediates prevalent during their measurement. For the purpose of elucidating structure-catalytic property relationships, the approach reported herein involving the use of well-defined thermally stable faceted oxide crystals has the potential to be broadly applicable within the field of bulk oxide catalysis.

Received 3rd September 2020, Accepted 10th November 2020

DOI: 10.1039/d0cy01732a

rsc.li/catalysis

## Introduction

Bulk metal oxides deliver promising performances in a range of industrial applications including catalysis,<sup>1,2</sup> gas sensing,<sup>3</sup> energy storage,<sup>4</sup> and photovoltaics,<sup>5–7</sup> with variations in oxide non-stoichiometry commonly used to tailor corresponding material function. For example, whereas stoichiometric titanium oxide absorbs light only in the UV range, understoichiometric titanium oxide (TiO<sub>2–x</sub>) exhibits extended absorption into the visible range, which is a feature that enables improvements in photocatalytic efficiency.<sup>8</sup> Cerium oxide is another case in point, with reversible changes in stoichiometry constituting the basis for its use as a buffer during lean–rich cycles in automotive exhaust treatment.<sup>9</sup> More specifically in

the context of this study, nickel oxide non-stoichiometry has been proposed to influence a variety of properties including p-type semi-conductivity,<sup>10,11</sup> electrochromism,<sup>12</sup> and catalytic performance.<sup>13,14</sup> Each nickel vacancy—the predominant defect type in Ni<sub>1-x</sub>O—is presumed to be compensated by two electron holes (h<sup>+</sup>) that act as charge carriers, endowing the material with p-type semi-conductivity and a change in color from green to black.<sup>12,15</sup>

While the precise defect structure of nickel oxide remains a subject of debate, its degree of non-stoichiometry has repeatedly been suggested as a determinant of catalytic performance. Li and coworkers were the first to propose a relationship between non-stoichiometric oxygen (NSO) density (defined in our study as moles of non-stoichiometric oxygen per mole total nickel) and ODHE catalytic performance.<sup>16</sup> They reported that thermal treatment at temperatures up to 700 °C led to concurrent decreases in NSO density—estimated using temperature programmed desorption (TPD)—and ethane conversion. The lack of ethene selectivity data at constant reaction temperature and ethane conversion in this study makes it challenging to interpret the

C ROYAL SOCIETY OF CHEMISTRY

**View Article Online** 

Department of Chemical and Biomolecular Engineering, University of Houston, 4726 Calhoun Rd., Houston, TX 77204, USA. E-mail: jrimer@central.uh.edu, ppbollini@uh.edu

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/ d0cy01732a

role of non-stoichiometric oxygen. It was also found that the non-stoichiometric oxygen content of the sample can be regenerated upon exposure to gas phase oxygen, meaning changes in NSO density can occur under ODHE reaction conditions. Lemonidou and coworkers tried to elucidate, albeit indirectly, the effect of NSO density on ODHE ethene selectivity by varying the niobium content in mixed Nb-Ni oxides.<sup>17-19</sup> Increasing Nb contents were found to result in decreasing NSO densities, and correlated with increasing ethene selectivities at constant conversion of ethane. The authors proposed that non-stoichiometric oxygen, being more electrophilic than lattice oxygen, plays a role in effecting oxidation to CO<sub>2</sub>, causing the reduction in NSO density to result in higher ethene selectivity.<sup>17,18</sup> It is important to note that the incorporation of Nb can lead to changes in a wide variety of physicochemical characteristics (some of which are identified below) thereby complicating interpretations in selectivity trends. A variety of other mixed metal oxide combinations including Ni-Ce,<sup>20,21</sup> Ni-W,<sup>22,23</sup> Ni-Al,<sup>24</sup> and Ni-Sn<sup>25,26</sup> have also been explored. Effects of aliovalent components have typically been interpreted under the hypothesis that the excess electron density resulting from the incorporation of high valence dopants contributes towards neutralizing holes present in the single component oxide, thereby decreasing the contribution of non-stoichiometric oxygen towards catalytic performance.14 Nickel oxide nonstoichiometry can also be tuned without the addition of a second component, merely through thermal treatment at high temperatures, as shown by Turky, who reported that electrical conductivities and surface excess oxygen densities (assessed using the hydrazine method) decrease with increasing calcination temperature between 300 and 700 °C.27

We emphasize that in each of these cases physicochemical characteristics apart from NSO density are inevitably varied, rendering inconclusive proposed correlations thereby between any one of these characteristics and ODHE performance. For example, Li and coworkers do not report the effect of thermal treatment on particle size, morphology, or crystallinity, only the relationship between NSO density and catalytic performance.<sup>16</sup> Turky, on the other hand, reports significant changes in surface area, crystallite size, and lattice parameter as a function of calcination temperature.<sup>27</sup> In other reports, incorporation of niobium was found to result not only in an evolution from sponge-like to plate-like morphology but also the potential formation of an active nickel niobate phase.<sup>17-19</sup> Analogous changes in surface coordination environment, the formation of new phases, and the agglomeration of dopants to form amorphous or crystalline foreign oxide domains are either conspicuously present, or at the very least challenging to eliminate in most prior literature attempting to decipher the role of non-stoichiometric oxygen indirectly through the incorporation of aliovalent dopants.<sup>17-26</sup> A key characteristic in this respect is the overall nickel oxide surface coordination environment, particularly in view of the fact that variations in surface coordination environment resulting from changes in distribution of exposed facets has been shown to be a critical factor affecting bulk metal oxide catalytic performance.<sup>28-30</sup> Thermal treatments used to vary NSO density can result (through sintering) in changes in particle sizes and exposed crystal facets,<sup>27,31,32</sup> and multicomponent oxides can exhibit domains that are highly heterogeneous not only from the standpoint of chemical composition but also of surface structure.<sup>33,34</sup> A second major limitation in existing reports is the fact that although NSO densities have been determined before exposure to ethane and oxygen, the effect of exposure to reaction conditions involving gas phase oxygen at high temperatures (typically greater than 400 °C) on NSO densities is typically not evaluated. For example, O2-TPD profiles in experiments reaching temperatures as high as 400 °C that can be reproduced upon cooling under oxygen suggest that changes in NSO density achieved using thermal treatments may potentially be partially or entirely erased upon exposure to oxygen and/or ethane at reaction temperatures.<sup>13</sup>

Although the effect of NSO density variations on ODHE performance has received significant attention in prior literature, less emphasis has been placed on attempting to exclusively vary NSO density under reaction conditions. In this study, we synthesize well-defined nickel oxide cubes exposing thermally stable {100} facets and demonstrate the ability to selectively tune NSO density under reaction conditions in order to assess its effect on ODHE ethene selectivity. In contrast with most prior literature reports that use control over crystal morphology directly for the purposes delivering improved catalytic of performance,<sup>30,35-39</sup> we use well-defined faceted oxide crystals for the selective alteration of specific, catalyticallyrelevant material properties that allow for the development of more rigorous structure-property relationships. To this end, we discuss, first, the synthesis of nickel oxide crystals with well-defined morphologies (cubes, octahedra, and trapezohedra), and their thermal stability. Next, we track, using three separate characterization techniques, changes in NSO density as a function of treatment temperature. Lastly, we report correlations between NSO density and ODHE catalytic performance. Overall, this study offers a template for addressing recurrent, persistent questions as to the nature, density, and catalytic function of defect sites in bulk oxide catalysis.

## Experimental methods

#### Materials synthesis

Nickel oxide cubes were prepared by a molten salt synthesis (MSS) using a reported protocol.<sup>40</sup> All materials were used as received. In a typical synthesis, 0.1 moles Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O ( $\geq$ 97.0%, Sigma-Aldrich), 0.5 moles KNO<sub>3</sub> ( $\geq$ 99.4%, J. T. Baker), and 0.5 moles NaNO<sub>3</sub> ( $\geq$ 99.6%, J. T. Baker) were ground with a mortar and pestle for 10 min. The mixture was transferred to an alumina crucible and calcined in a muffle furnace at 550 °C for 1 h with a 2.5 °C min<sup>-1</sup> ramp rate. After

cooling down to room temperature, alkali salts were removed by washing with ca. 2 L of deionized (DI) water (Aqua Solutions RODI water purification system, >18.2 M $\Omega$ ) combined with suction-filtration, followed by drying at 60 °C overnight. The as-synthesized oxide was divided into five fractions, each of which was calcined in a muffle furnace (Nabertherm, LE 6/11) under 100 cm<sup>3</sup> min<sup>-1</sup> of N<sub>2</sub> flow at different temperatures for 5 h with a 2.5 °C min<sup>-1</sup> ramp rate. Samples were labeled  $NiO_{400},\ NiO_{500},\ NiO_{600},\ NiO_{800},$  and Ni1000 where the subscript indicates the post-synthesis thermal treatment temperature in °C. Nickel oxide crystals with octahedral and trapezohedral habit were synthesized using a similar procedure as that for cubes, but by replacing alkali nitrates with 1 mole LiNO<sub>3</sub> in the case of octahedra, and a mixture of KCl and NaCl (0.5 moles each) in the case of trapezohedra.

#### Materials characterization

Scanning electron microscopy (SEM) images were acquired with a LEO 1525 FEG system operated at 3 kV. Powder X-ray diffraction (PXRD) was performed using a SmartLab Rigaku diffractometer with a Cu K $\alpha$  source ( $\lambda$  = 1.5406 Å). The diffraction patterns were analyzed using the Rigaku PDXL software equipped with the ICDD database. Nitrogen physisorption was performed at 77 K in a Micrometrics 3Flex system. Prior to N<sub>2</sub> physisorption, approximately 0.5 grams of sample were degassed under 140 mTorr vacuum at 250 °C for 12 h. The UV-vis diffuse reflectance spectrum (DRS) of samples was measured with an Agilent Cary 5000 spectrophotometer equipped with a diffuse reflectance accessory using a Spectralon plate as a reference. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI 5800 ESCA system (Physical Electronics) equipped with a standard achromatic Al Ka X-ray source (1486.6 eV) operating at 300 W (15 kV and 20 mA) and a concentric hemispherical analyzer. Data were collected at a 45° takeoff angle, and measured spectra were analyzed using the MultiPak program, with the C1s peak calibrated at 284.8 eV.

Temperature programmed desorption (TPD) and H<sub>2</sub>temperature programmed reduction (TPR) were carried out in a fixed-bed reactor where the outlet gas composition was monitored using an MKS Cirrus 2.0 quadrupole mass spectrometer. In a typical TPD measurement, 0.25 grams of sample were loaded in a quartz tube (1 cm internal diameter with a quartz frit) and 50 cm<sup>3</sup> min<sup>-1</sup> He (carrier) and 1 cm<sup>3</sup> min<sup>-1</sup> Ar (internal standard) were fed at room temperature. Once all mass/charge signals were stable, the temperature was increased to 1100 °C at a rate of 7 °C min<sup>-1</sup>. For testing samples pre-exposed to either oxygen or reaction conditions (ethane + oxygen), pre-TPD treatments were carried out by exposing the catalyst to either 26 kPa O2 at 450 °C or 5 kPa  $C_2H_6/5$  kPa  $O_2$  at 400 °C for 30 min, then cooling to room temperature prior to each TPD measurement. In a typical H<sub>2</sub>-TPR measurement, 20 mg of sample was pretreated under 28 cm<sup>3</sup> min<sup>-1</sup> He and 1 cm<sup>3</sup> min<sup>-1</sup> Ar at 150 °C for 30 min

Catalysis Science & Technology

before 3 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> was added to this stream. The temperature was then increased to 700 °C at a ramp rate of 10 °C min<sup>-1</sup>.

#### Catalytic testing

Helium, oxygen, ethane, and ethene gas cylinders (Matheson, UHP grade) were used as purchased. Gas flows were controlled by mass flow controllers (MKS Instruments, GE50A) with external calibration, and the flow rates were measured with a bubble flow meter each time before reaction. DI water was injected into the reaction lines using a syringe pump (KD Scientific, model 100) during reaction rate measurements. All gas lines were heated above 100 °C with heating tape to avoid condensation.

The reaction setup consisted of two parallel gas lines—a pretreatment line and a reaction line—that could be interchanged using a four-port valve (VICI-Valco, 400 psi). The gas composition of each line was analysed using a gas chromatograph (GC) (Agilent 7890B) equipped with a GS-CarbonPLOT column (30 m, 0.32 mm, 1.50  $\mu$ m) whose outlet was split into a flame ionization detector (FID) and a thermal conductivity detector (TCD) with a two-way splitter (Agilent, G3184-60065). Ethane and ethene were quantified using the FID signal, and O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O were quantified using the TCD (CO formation, if any, stayed below the detection limits of this study).

The sample tube was heated using an insulated singlezone furnace (Applied Test Systems, Series 3210) with a thermocouple (Omega Engineering, KMQXL-062U-15) placed at the top of the catalyst bed. The thermocouple was connected to an integrated temperature controller (Watlow, EZ-Zone PM) to control bed temperature. A pressure transducer (Omega Engineering, PX32B1-050AV) was used to record the pressure above the catalyst bed.

Prior to reaction, catalyst samples were pressed, crushed, and sieved (40-80 mesh). The pellets were then mixed with quartz sand (40-80 mesh, acid washed and calcined at 1000 °C) in a weight ratio ranging between 1:1 and 1:10. Each sample was loaded into a 4 mm inner diameter quartz tube and supported by a quartz frit. The quartz tube was mounted into the center of the furnace; the sample temperatures reported are those at the top of the catalyst bed. During the pretreatment step the reactor was heated to 450 °C at a ramp rate of 3 °C min<sup>-1</sup> under He and then pretreated under a 26 kPa O2 in He flow at 450 °C for 30 min. The reactor was purged under He for 1 h while the sample temperature was ramped to the target reaction temperature. Then, the reactant feed flow was stabilized in the reaction line and its composition was analyzed by gas chromatography, before being introduced to the reactor by switching the four-port valve and reanalyzed. The carbon balance (%C), ethane conversion  $(X_{C_2H_4})$ , and ethene carbon selectivity  $(S_{C_2H_4})$  were calculated using the following equations:

$$%C = \frac{F_{C_2H_4} + F_{CO_2}/2}{F_{C_2H_6, \text{feed}} - F_{C_2H_6}}$$
(1)

$$S_{C_2H_4} = \frac{F_{C_2H_4}}{F_{C_2H_4} + F_{CO_2}/2}$$
(3)

where  $F_i$  represents the molar flow rate of each species (ethene, CO<sub>2</sub>, and ethane) measured at the reactor outlet, and  $F_{C_2H_6,feed}$  represents the molar flow rate of ethane fed to the reactor. The factor of 2 in eqn (3) reflects the fact that two CO<sub>2</sub> molecules are formed from one C<sub>2</sub>H<sub>6</sub> molecule. Conversion and selectivity are reported as steady state values. Reaction runs in the absence of catalyst conducted at the corresponding ethane and oxygen residence times at 500 °C exhibited negligible ethane conversions, eliminating the need for blank tube subtractions. Negligible changes in ethane conversion and ethene selectivity over NiO cubes were observed in extended runs lasting 24 h.

## **Results and discussion**

# Synthesis and characterization of thermally stable NiO crystals

Nickel oxide crystals with three well-defined morphologies were synthesized using MSS techniques reported previously.<sup>40,41</sup> Synthesis mixtures prepared with NaNO<sub>3</sub>:KNO<sub>3</sub> (1:1 molar ratio), LiNO<sub>3</sub>, or NaCl:KCl (1:1 molar ratio) resulted in cubic, octahedral, or trapezohedral crystals, respectively. The phase purity of these products was confirmed using PXRD, with only diffraction peaks corresponding to the cubic-structured NiO phase (space group  $Fm\bar{3}m$ ) being observed (Fig. S1<sup>†</sup>).

Cubes, octahedra, and trapezohedra expose {100}, {111}, and {311} facets, respectively (Scheme S1<sup>†</sup>), and result in notable differences in surface coordination numbers. Whereas the exposure of {100} surfaces results in surface coordination numbers of 5 for both surface nickel and surface oxygen, both {111} and {311} facets result in significantly lower coordination numbers-three for either oxygen or nickel (depending on surface termination) in the case of {111} surfaces, and 2 for atoms in the topmost layer (nickel or oxygen) for  $\{311\}$  surfaces. Qualitatively, one may expect  $\{100\}$ nickel oxide surfaces having a lower degree of coordinative unsaturation to be more stable compared to  $\{111\}$  and  $\{311\}$ surfaces-an expectation borne out in calculated surface energies for defect-free {111} surfaces that are more than twofold greater than those of the corresponding {100} surfaces.<sup>42,43</sup> Moreover, pristine {111} and {311} surfaces terminated by single layers of nickel or oxygen are comprised of alternately charged planes that in theory result in a dipole moment perpendicular to the surface; divergent surface energies resulting therefrom are presumed to be circumvented through either surface reconstruction or adsorption of foreign aliovalent impurities.<sup>36</sup> The preservation of particle morphology in the case of cubes, reflected in the sharp edges and well-defined terraces observed upon thermal treatment up to 1000 °C (Fig. 1a-c), in contrast with octahedra



Fig. 1 SEM images of as-synthesized (a) cubic, (d) octahedral, and (g) trapezohedral NiO crystals, and corresponding images after thermal treatments at increasing post-synthesis calcination temperatures of (b, e and h) 700 °C and (c, f and i) 1000 °C for 5 h. Scale bars equal 1  $\mu$ m.

(Fig. 1d–f) and trapezohedra (Fig. 1g–i) that exhibit a disappearance of vertices and edges, is consistent with expectations based on the coordination environment of pristine, defect-free, unreconstructed surfaces.

We note that although qualitative trends in crystal stability reported here can be rationalized on the basis of coordination environments of defect-free surfaces, we know for a fact that NSO densities evolve upon thermal treatment, implying that the relative stabilities of defect-containing surfaces, rather than defect-free surfaces would likely determine trends noted in Fig. 1. Complex trends in surface energy as a function of NSO density and temperature make it challenging to establish the basis for the greater relative thermal stability of nickel oxide cubes.42,43 We clarify that the basis for the higher thermal stability of nickel oxide cubes, the elucidation of which requires a more detailed understanding of surface energy variations as a function of both treatment temperature and defect density, is not the focus of our study. The higher relative stability of cubes-a phenomenological observation in the context of our investigation-provides a material uniquely suited to altering, exclusively, NSO density using hightemperature thermal treatment protocols. We note that unlike prior literature where methods for varying NSO density also tend to impact other physicochemical characteristics (vide supra), the preservation of cubic morphology in our case is accompanied by imperceptible changes in degree of crystallinity (Fig. S2<sup>†</sup>), no apparent changes in particle morphology (Fig. S3<sup>†</sup>), and only minor changes in BET surface area (Fig. S5 and Table S1<sup>†</sup>). Moreover, particle size distribution analyses of samples treated at 400 and 1000 °C suggest a mere 22% increase in particle size upon thermal

#### Paper

**Catalysis Science & Technology** 

treatment (Fig. S4<sup>†</sup>). MSS-derived NiO cubes, unlike more complex materials that undergo significant changes in surface area, crystallite size, and lattice parameter(s) as a function of calcination temperature,<sup>27</sup> provide a platform for tuning NSO density using thermal treatments, and assessing its role in effectuating selective as well as unselective alkane oxidation turnovers. We discuss next the use of characterization techniques that provide either qualitative or quantitative insights into NSO density of NiO cubes.

#### Tuning NiO non-stoichiometry under reaction conditions

UV-visible spectroscopy. Color has commonly been used as a marker of NiO non-stoichiometry, with reversible transitions between black and green bleached states being possible not only in response to changes in NSO density by oxygen exchange but also through the application of a voltage across the oxide surface.44-46 Adsorption of oxygen onto greenish-yellow stoichiometric nickel oxide results in darkening of the samples, as noted previously by several groups.<sup>12,47-49</sup> Consistent with these reports, thermal treatment protocols used herein result in an evolution in coloration from black to green (Fig. 2a), consistent with reductions in NSO density with increasing treatment temperature. This evolution in color can be represented more quantitatively in the form of absorption spectra in the visible range. Irrespective of thermal treatment temperature, the samples exhibit two broad absorption bands centered around 417 and 700 nm (Fig. 2b) that have been consistently observed in prior literature, 12,47,48,50 and correspond to d-d electron transitions of octahedrallycoordinated Ni<sup>2+</sup> ions in the crystal lattice.<sup>47</sup> Higher treatment temperatures resulted in similar absorbance corresponding to these two bands, but lower absorbance within the 500-600 nm range in the green-yellow region of the visible spectrum. An



Fig. 2 (a) Photographs of nickel oxide samples exhibiting a progressive color change after high-temperature thermal treatments for 5 h under N<sub>2</sub> (treatment temperatures, in °C, indicated as subscripts), and (b) corresponding visible absorption spectra calculated from UV-vis diffuse reflectance spectrum measurements using a Kubelka–Munk transformation.

increase in background absorbance in this region has been associated with an increase in NiO NSO content by several authors. For example, Newman and Chrenko noted similar changes in the UV-vis spectrum upon deliberate introduction of oxygen achieved through exposure of NiO single crystals to air at 1200 °C.<sup>12</sup> Similar increases in background absorption were also noted by Haber and Stone upon oxygen adsorption at 20 °C,<sup>47</sup> and by Larkins and Fensham upon oxygen adsorption equivalent to merely 1.85% of monolayer coverage.<sup>48</sup> We note that the origin of this background absorption, although previously discussed in the context of Ni<sup>3+</sup> ions, excess oxygen, holes, and impurities,<sup>12,31,33</sup> remains as-yet unresolved.

Also, absorption spectra, although consistent with expectations based on existing literature, provide only qualitative insights into NSO density. To obtain quantitative trends into NSO density, we used TPD and TPR measurements, as described in the following sections.

Temperature programmed desorption. The evolution in NSO density as a function of treatment temperature can be monitored using  $O_2$ -TPD measurements in which the molar flow rates of  $O_2$  desorbing from the samples are quantified upon subjection to a pre-set temperature profile under inert gas flow. Measurements of  $O_2$ -TPD have been reported over a wide range of mixed metal oxide catalysts, and reveal information pertaining not only to the density of oxygen moieties but also their speciation.<sup>51–53</sup> Specifically, in the case of single and multicomponent nickel oxide materials,  $O_2$ -TPD has been applied to quantify non-stoichiometric oxygen largely predicated on the tacit assumption that the oxide becomes fully stoichiometric upon exposure to high temperatures.<sup>18,19</sup>

Such loss of non-stoichiometric oxygen can be represented using the following equation:

$$Ni_{1-x}O \rightarrow (1 - x_{TPD}) NiO + (x_{TPD}/2) O_2$$
 (4)

where  $x_{\text{TPD}}/(1 - x_{\text{TPD}})$  represents the moles of nonstoichiometric oxygen (excess O) per mole of nickel (or equivalently, of the respective stoichiometric Ni), and can be calculated from O<sub>2</sub>-TPD experiments using the equation:

NSO density (TPD) = 
$$\frac{x_{\text{TPD}}}{1 - x_{\text{TPD}}} = \frac{(M_{\text{Ni}} + M_{\text{O}}) \times N_{\text{O}_2,\text{desorbed}}}{2m + M_{\text{O}}N_{\text{O}_2,\text{desorbed}}}$$
 (5)

where  $N_{O2,desorbed}$  represents the total moles of  $O_2$  desorbed in a complete TPD experiment performed on a sample of mass *m* (derivation in section S3 of ESI†), and  $M_{Ni}$  and  $M_O$ represent the atomic weights of Ni and O, respectively.

Oxygen desorption onset temperatures increase monotonically with increasing treatment temperature (Fig. 3a), with onset temperatures being lower than the corresponding treatment temperatures (Table S1†) (except for the sample treated at 400 °C). Oxygen readsorption onto thermally treated samples may contribute to these lower desorption onset temperatures, as indicated by much closer correspondence between desorption onset and treatment temperatures for the sample maintained under inert gas flow after the 600 °C treatment instead of being exposed to air



Fig. 3 (a) O<sub>2</sub>-TPD profiles of as-synthesized Ni<sub>1-x</sub>O and samples prepared at increasing treatment temperatures (indicated as subscripts in °C) for 5 h at a 2.5 °C min<sup>-1</sup> ramp rate. Data are stacked arbitrarily on the *y*-axis for visual clarity. Data for NiO<sub>700</sub> are multiplied by 2. Scale bar:  $1 \times 10^{-6}$  mol O<sub>2</sub> per g Ni per min. (b) NSO densities are estimated by inserting integrated O<sub>2</sub> desorption rates over time into eqn (5).

(Fig. S6†); moreover, this sample, which was isolated from ambient conditions post-thermal treatment and pre-TPD, also exhibits a lower total moles of  $O_2$  desorbed per gram of sample compared to the one exposed to ambient conditions, consistent with the readsorption of  $O_2$  upon exposure to atmospheric conditions.<sup>16</sup> These results point to the prevalence of complex  $O_2$  adsorption–desorption phenomena that occur during the thermal treatment protocols used in our study. For the sake of consistency, all samples discussed later were treated for 5 h under inert gas flow and were exposed to ambient conditions prior to TPD and ODHE experiments.

TPD temperatures have commonly been used to infer oxygen speciation.<sup>16,54,55</sup> For example, Chen et al. proposed that two forms of non-stoichiometric oxygen exist on bulk nickel oxide calcined at 500 °C $-\alpha$  oxygen species that desorb between 300 and 450 °C, and  $\beta$  oxygen species that desorb between 450 and 620 °C.16 Mobile, extra-lattice, adsorbed oxygen was interpreted to desorb at lower temperatures ( $\alpha$ oxygen species), and lattice oxygen was interpreted to desorb at higher temperatures ( $\beta$  oxygen species). Seiyama and coworkers tentatively interpreted four distinct oxygen desorption peaks ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ) with increasing desorption temperatures from 30 to 600 °C, with  $\alpha$  and  $\beta$  species corresponding to molecular oxygen (i.e. physisorbed O2 and  $O_2^{-}$ ) and  $\gamma$  and  $\delta$  peaks corresponding to  $O^{-}$  adsorbed on two different sites.54 A majority of the oxygen desorption in Seiyama's work occurred below 400 °C,54 i.e., at temperatures lower than those reported by other groups,<sup>14,56,57</sup> including ours. Well-resolved desorption peaks were not observed in our experiments, in contrast with some of these literature reports that exploit such resolution to elucidate oxygen speciation. Differences in synthetic procedures and postsynthesis treatment protocols used may account for some of these differences. For instance, low temperature oxygen adsorption followed by evacuation at 0 °C carried out prior to the TPD experiments, as reported by Seiyama and coworkers,

could have resulted in the generation of specific oxygen moieties that desorb at lower temperatures.

Bulk oxygen desorption is a possible contributor to the broadness of the TPD peaks in Fig. 3, presumably with surface oxygen desorption preceding bulk oxygen desorption. The non-stoichiometric oxygen in the NiO<sub>400</sub> sample of our study would theoretically correspond to 4.78 monolayers of excess oxygen (assuming surface nickel density to be 1.15 ×  $10^{19}$  surface nickel per m<sup>2</sup>),<sup>31</sup> indicating that both surface and bulk oxygen are desorbed upon TPD between 400 and 1000 °C. Similar TPD profiles have been reported for other bulk metal oxides, such as perovskites (e.g. LaMnO<sub>3</sub> and SmCoO<sub>3</sub>), where the breadth of the TPD peaks spans 600  $^{\circ}$ C, and have been attributed to bulk oxygen desorption.58 NSO densities calculated by integrating No, desorbed areas and applying eqn (5) decrease with increasing treatment temperatures (Fig. 3b), qualitatively consistent with UV-vis spectroscopy data (Fig. 2b). Although a concurrent evolution in Ni<sup>3+</sup> density upon thermal treatment remains plausible, nickel oxidation states remained challenging to access through characterization methods employed in this study.

The as-synthesized NiO cubes (without thermal treatment) desorbed 1.04 mg  $O_2$  per m<sup>2</sup>, similar to the TPD-derived value of 0.9 mg  $O_2$  per m<sup>2</sup> reported by Lemonidou and coworkers for NiO prepared by the direct decomposition of nickel nitrate.<sup>17</sup> densities decreased with increasing treatment NSO temperature (Fig. 3b), with negligible NSO density measured for the sample treated at 1000 °C. TPD protocols used here seem to eliminate residual non-stoichiometric oxygen after thermal treatment, as indicated by the UV-vis spectrum of the post-TPD sample treated at 1000 °C that appears similar to that before TPD (Fig. S7<sup>†</sup>). Although these characterization data show that TPD protocols render all samples subjected to the measurement more stoichiometric in nature, they do not provide any quantitative indications of the final degree of (non)stoichiometry after TPD (Fig. S7b<sup>+</sup>). Existing literature provides little evidence as to the degree of stoichiometry of samples post-TPD, leaving open the possibility of incomplete oxygen desorption, and therefore of underestimations in NSO density when applying this widely used technique. In fact, the achievement of stoichiometric nickel oxide samples post-TPD has not been proven, or even proposed from either a thermodynamic or kinetic standpoint. Next, we use TPR experiments performed in the presence of gas phase molecular hydrogen to address some of these concerns relating to a potentially incomplete non-stoichiometric oxygen removal.

**H**<sub>2</sub>-**Temperature programmed reduction.** TPD protocols carried out in inert environments are driven by differences in Gibbs free energies between the non-stoichiometric and the stoichiometric surfaces/phases combined with gas phase oxygen. These thermodynamic driving forces may not necessarily lead to stoichiometric oxides within temperature ranges accessible in typical TPD experiments. In contrast, TPR experiments carried out in the presence of gas phase hydrogen are driven by Gibbs free energy differences between gas phase hydrogen and water, in addition to those between non-

#### Paper

stoichiometric (oxide) and stoichiometric (metal) surfaces, thereby potentially presenting greater thermodynamic driving forces for NSO removal at identical temperatures. This greater propensity towards reduction under hydrogen flow is reflected in the fact that complete reduction to metallic nickel below 600 °C has either been suggested,<sup>59,60</sup> or evidenced directly in the literature, for example using *in situ* time-resolved XRD.<sup>61</sup> Complete reduction under hydrogen is also reinforced by the close agreement between H<sub>2</sub> TPR-derived NSO densities and those obtained by Bunsen–Rupp titrations that assume a 1:1 Ni<sup>3+</sup>:NSO ratio.<sup>62</sup> Assuming complete reduction to metallic nickel below 600 °C, the following equation can be used to represent the reduction process:

$$Ni_{1-x}O + H_2 \rightarrow (1 - x_{TPR}) Ni + H_2O$$
(6)

The moles of non-stoichiometric oxygen per mole of nickel can be calculated using the following equation:

NSO density (TPR) = 
$$\frac{x_{\text{TPR}}}{1 - x_{\text{TPR}}}$$
 (7)  
=  $\frac{(M_{\text{Ni}} + M_{\text{O}}) \times N_{\text{H}_2,\text{consumed}} - m}{m - M_{\text{O}}N_{\text{H}_2,\text{consumed}}}$ 

where  $N_{\rm H2,consumed}$  represents the total moles of  $\rm H_2$  consumed during the  $\rm H_2$ -TPR run (the derivation is provided in section S3<sup>†</sup>).

NiO samples show smaller differences in reduction onset temperature compared to  $O_2$  desorption onset temperatures (Fig. 4a and 3a), with the latter varying by more than 100 °C over the range of treatment temperatures used herein. Integrated H<sub>2</sub> uptake values incorporated into eqn (7) result in NSO densities that decrease from 0.25 to 0.01 with increasing treatment temperatures. Importantly, H<sub>2</sub>-TPR derived NSO densities are significantly larger than corresponding values derived from TPD profiles (Fig. 3b), consistent with the incomplete desorption of nonstoichiometric oxygen upon exposure to inert gas flow up to



**Fig. 4** (a) H<sub>2</sub>-TPR profiles and (b) non-stoichiometric oxygen densities estimated from H<sub>2</sub>-TPR measurements for thermally treated nickel oxide samples (subscripts represent treatment temperatures in °C). In (a), data are stacked on the *y*-axis and the scale bar equals  $5 \times 10^{-4}$  mol H<sub>2</sub> per g Ni per min.

1050 °C, pointing to the need for caution in using solely either UV-vis spectra or temperature programmed desorption to quantify NSO density. We note that the lack of standard oxide samples that are (*a priori*) known to be stoichiometric makes precise quantitative determinations of NSO density for bulk metal oxides highly challenging; however, access to a well-defined material composition post characterization metallic nickel in this case—may help circumvent this limitation. In summary, differences between TPD and TPRderived NSO densities (Fig. 3b *versus* Fig. 4b) emphasize the importance of not relying solely on TPD measurements, or exclusively on any one *ex situ* characterization technique, when quantifying bulk metal oxide NSO density.

#### Evolution in NSO density under reaction conditions

ODHE reactions are commonly interpreted within the context of Mars-van Krevelen (MvK) redox cycles, with hydrogen abstraction and water desorption steps constituting the reduction half of the cycle, and surface oxygen regeneration steps constituting the oxidation half of the catalytic cycle.63,64 The possible depletion and regeneration of NSO within a single MvK cycle creates the need for assessing its density upon exposure to ethane and/or oxygen under reaction conditions. Skoufa et al., for example, reported a 50% drop in TPD-derived NSO density of bulk nickel oxide upon exposure to ethane and oxygen at 400 °C.19 Changes in NSO density, albeit only of a qualitative nature, were also reported by Caps and coworkers, who noted a change in color from black (non-stoichiometric) to green (more stoichiometric) upon exposure to ODHE reaction conditions at 400 °C.65 The plausibility of NSO loss within MvK cycles, combined with previous studies reporting NSO desorption under reaction conditions, necessitates a comparison of NSO densities before and after exposure to oxygen and oxygen-ethane mixtures at reaction temperatures. TPD profiles for samples treated at 600 °C that change only minimally upon exposure to oxygen (curve ii, Fig. 5a) and oxygen-ethane mixtures (curve iii, Fig. 5a), and NSO densities that are significantly less sensitive to the presence of oxygen (ii, Fig. 5b) or oxygen-ethane mixtures under reaction conditions (iii, Fig. 5b) than to high-temperature thermal treatments suggest that the protocols used in our study can be used to control NSO densities not just ex situ, but also in situ under ODHE conditions. Crucially, this insensitivity of NSO density to the presence of ethane and oxygen enables an assessment of its density on catalytic performance in integral packed bed catalytic experiments resulting in reactant concentrations that change significantly along the length of the bed. In the following section, we use this control over NSO density under reaction conditions, which is atypical for bulk oxide materials,<sup>19,65</sup> to manipulate ODHE catalytic performance.

#### Effect of NSO density on ODHE catalytic performance

Ethene selectivity at isoconversion. Here we examine the effect of NSO density on nickel oxide ODHE performance at



**Fig. 5** (a)  $O_2$ -TPD profiles of nickel oxide thermally treated at 600 °C (i) before, and after exposure to (ii) 26 kPa  $O_2$  at 450 °C for 30 min, and (iii) to 5 kPa  $O_2$  and 5 kPa  $C_2H_6$  at 400 °C for 30 min. Data are stacked on the *y*-axis. (b)  $O_2$ -TPD derived NSO densities as a function of treatment temperature. The error bars for NiO<sub>400</sub> were obtained from two individual measurements.

ethane isoconversion. Our findings reveal a direct correlation between NSO density and ethene selectivity, both of which decrease monotonically with increasing treatment temperature (Fig. 6). Ethene selectivities must be compared at similar ethane conversions due to possible contributions from secondary oxidation reactions of ethene. We note that ethene selectivities that track qualitatively with NSO density are observed over a wide range of reaction temperatures (400-500 °C), and these trends persist upon varying ethane and oxygen partial pressures (Fig. 6). These favorable effects of NSO density on ethene selectivity contrast with suggestions made previously in the literature based on the use of complex



**Fig. 6** Ethene carbon selectivity (colored bars, left *y*-axis) and corresponding TPR-derived NSO densities (white diamonds, right *y*-axis) as a function of thermal treatment temperature measured at (a) 2.5, (b) 10, and (c) 16% ethane conversion. These conversions were achieved by adjusting space times for each sample and reaction condition. The three sets of data correspond to the following ODHE conditions: (a) 400 °C,  $P(C_2H_6) = 15$  kPa,  $P(O_2) = 5$  kPa; (b) 450 °C,  $P(C_2H_6) = 10$  kPa,  $P(O_2) = 5$  kPa; and (c) 500 °C,  $P(C_2H_6) = 10$  kPa,  $P(O_2) = 10$  kPa.

mixed metal oxides - a discrepancy that may be attributable to the incorporation of active secondary oxide phases<sup>22,66</sup> or extra-lattice surface species,<sup>25</sup> a modification of surface acidbase properties, or a decrease or increase, respectively, in the number of nickel-oxygen or Ni-O-M pairs.14 Our data, measured under conditions with negligible contributions from secondary reactions (vide infra), necessitate the presence of at least two distinct types of sites that mediate ethene and CO<sub>2</sub> formation, and whose relative surface densities change with increasing treatment temperature. We note that differences in catalytic properties presented herein are unlikely to be a consequence of residual alkali metal content, with surface potassium content being below XPS detection limits, and that of sodium being less than 1.4% (Table S2<sup>+</sup>). The low percentages of surface alkali metal content, combined with the absence of a correlation between their content and ODHE catalytic performance make nonstoichiometric oxygen, rather than alkali metal content, the more likely determinant of ODHE performance.

Possibilities for the identity of these sites include active oxygen moieties differing in electrophilicity, as has commonly been proposed for C-H bond activation in bulk oxide catalysis.<sup>17,67,68</sup> The roles of these different types of active oxygen moieties can be hard to elucidate,<sup>69-72</sup> and does not constitute the focus of this study. Other clues as to the nature of these active sites on nickel oxide, however, do exist in the literature. For instance, Heracleous and Lemonidou found that the rates of ODHE and total oxidation were inhibited to different extents with increasing water co-feed pressure, possibly due to differences in water reaction orders for the selective and unselective reactions.<sup>18</sup> Density function theory (DFT) calculations have been used to study C-H abstraction steps over nickel-oxygen pairs that form ethyl fragments on the nickel atoms, and surface oxygen sites that form ethoxides, the two of which may have different relative susceptibilities towards subsequent C-H and C-C bond cleavage steps.<sup>73,74</sup> A combination of nickel-oxygen pair sites and oxygen sites, the relative abundance of which evolves with treatment temperature, represents one possible example of the identities of active sites responsible for the selectivity trends in Fig. 6.

The need for more accurate active site densities and turnover frequencies. Elucidating the identity and mechanistic role of different sites involved in nickel oxidecatalyzed dehydrogenation (to ethene) and oxidation (to  $CO_2$ ) may be aided by the availability of kinetic data at the level of rate constants. Direct measurement of dehydrogenation and oxidation rates are complicated, in part, by potential contributions from secondary oxidation reactions that render measured ethene formation rates to be lower bounds on ODHE rates (Scheme 1). Ethene selectivities that decrease with increasing ethane conversion (Fig. S8†) are consistent with the reaction network shown in Scheme 1, in which increasing contributions from ethene oxidation  $(r_3)$  relative to the oxidative dehydrogenation  $(r_1)$  can be envisioned with increasing conversion. These increasing contributions from

Paper



Scheme 1 Proposed reaction network for ethane oxidative dehydrogenation and total oxidation involving both primary and secondary pathways for  $CO_2$  formation in the presence of  $O_2$ .

secondary reactions are also reflected in ethene formation rates that decrease with increasing residence time (Fig. S9<sup>†</sup>). CO<sub>2</sub> formation rates, on the other hand, must necessarily increase with residence time due to a greater relative preponderance of secondary reactions at higher conversions achieved at longer residence times. CO2 formation rates that decrease, rather than increase, with residence time, on the other hand (Fig. S9<sup>†</sup>), indicate that the changes in formation rates, and hence selectivities, as a function of residence time may be a consequence of product inhibition rather than being a result of gradients in ethene partial pressure. Negligible contributions from secondary oxidation reactions are also reinforced by the similar oxidation rates measured for ethane and ethene at equivalent reactant pressures (Fig. S10<sup>†</sup>). These similar oxidation rates, combined with the low ethene to ethane ratios prevalent at the low conversions used in the rate measurements (i.e. less than 1% ethane conversion) suggest the products formation are almost exclusively from primary reactions. Consistent with these findings, co-feeding 1-10 kPa water results in ethene and CO2 formation rates that are lower than those measured in the absence of water co-feeds. These formation rates are also rather insensitive to residence time (Fig. S11<sup>†</sup>) resulting from a flattening of water partial pressure gradients through the bed (Scheme S2, ESI<sup>†</sup>). Inhibition of oxidation rates by water have been noted previously over nickel oxide,<sup>17,75</sup> and also for light alkane ODH over other catalysts, such as supported vanadium and molybdenum oxides.<sup>76-78</sup> Water co-feeds can therefore be used to artificially create differential beds that reveal rates of primary ODHE and oxidation, which can then be compared as a function of NSO density. The ratios of primary ODHE to oxidation rates  $(r_1/r_2)$  in the presence of water co-feeds that are rather invariant in NSO density except for the sample with the lowest NSO density (Fig. S12<sup>†</sup>) suggest that monotonic trends in ethene selectivity noted in the absence of water co-feeds (Fig. 6) may not necessarily translate to reaction conditions resulting in surfaces with large fractional hydroxyl coverages. The non-monotonic trends in the ratio of primary reaction rates also point to the need for developing characterization techniques that allow for a more accurate characterization of surface active site density. Moreover, the differences in trends in ethene selectivity as a function of NSO density in the presence and absence of water co-feeds point to the need for more caution

in interpreting structure-catalytic property relationships using phenomenological measures like selectivity, rather than the rate constants.

## Conclusions

Well-defined nickel oxide cubes exposing {100} facets were used to exclusively alter the non-stoichiometric oxygen (NSO) density while maintaining the degree of crystallinity, particle size, and morphology. These cubes, synthesized using molten salt techniques, were found to be significantly more resistant to thermal treatments compared to their octahedral and trapezohedral counterparts, rendering them amenable to high temperature treatments used to control NSO density. UV-vis spectroscopy, TPD, and H2-TPR all suggest decreasing NSO densities with increasing treatment temperature. Importantly, NSO density variations upon exposure to ethane and oxygen are smaller than those achievable using thermal treatment protocols employed in our study, meaning that control over NSO density is enabled not only ex situ, but also in situ under ODHE reaction conditions. We show that ethene selectivities at isoconversion track with NSO density over a wide range of temperatures and reactant pressures, thereby providing a lever for controlling catalytic performance. Relative rates of primary reactions on surfaces with greater fractional hydroxyl coverages, on the other hand, were found to be rather insensitive to NSO density except at the lowest value achievable, suggesting that the selectivity control achieved in our study (and proposed in prior literature) may only be achievable under specific constraints, for example, low hydroxyl coverages.

Using the role of non-stoichiometric oxygen in ODHE as an example, this study emphasizes three specific, disparate aspects of bulk oxide catalysis: (1) the importance of synthesizing well-defined oxide materials that allow for the exclusive variation of a small number of physicochemical characteristics, (2) the utility of exploiting multiple characterization techniques in quantifying these characteristics, and (3) the need for rigorously measured reaction rates as a prerequisite for clearly elucidating active site requirements for both selective and unselective steps in partial oxidation reaction networks. We envision that the approach used here for elucidating structure-catalytic property relationships via the combination of advanced synthesis, characterization, and kinetic analysis may be applied more broadly within the domain of bulk oxide catalysis.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

PB acknowledges UH startup funds that were used to set up the reactor used in this study. JDR acknowledges support from The Welch Foundation (Award E-1794).

## References

- 1 J. C. Védrine, ChemSusChem, 2019, 12, 577-588.
- 2 W. Huang, Acc. Chem. Res., 2016, 49, 520-527.
- 3 N. Barsan, D. Koziej and U. Weimar, *Sens. Actuators, B*, 2007, **121**, 18–35.
- 4 S. Fang, D. Bresser and S. Passerini, *Adv. Energy Mater.*, 2020, **10**, 1902485.
- 5 C. T. Sah, IEEE Trans. Electron Devices, 1964, 11, 324-345.
- 6 M.-J. Lee, S. I. Kim, C. B. Lee, H. Yin, S.-E. Ahn, B. S. Kang, K. H. Kim, J. C. Park, C. J. Kim, I. Song, S. W. Kim, G. Stefanovich, J. H. Lee, S. J. Chung, Y. H. Kim and Y. Park, *Adv. Funct. Mater.*, 2009, **19**, 1587–1593.
- 7 A. Pérez-Tomás, A. Mingorance, D. Tanenbaum and M. Lira-Cantú, *Futur. Semicond. Oxides Next-Generation Sol. Cells*, 2018, pp. 267–356.
- 8 N. Serpone, J. Phys. Chem. B, 2006, 110, 24287-24293.
- 9 J. Kašpar, P. Fornasiero and M. Graziani, *Catal. Today*, 1999, **50**, 285–298.
- 10 S. Mrowec and Z. Grzesik, J. Phys. Chem. Solids, 2004, 65, 1651-1657.
- 11 A. Bielański, J. Dereń, J. Haber and J. Słoczyński, *Trans. Faraday Soc.*, 1962, **58**, 166–175.
- 12 R. Newman and R. M. Chrenko, *Phys. Rev.*, 1959, **114**, 1507–1513.
- 13 T. Chen, W. Li, C. Yu, R. Jin and H. Xu, *Stud. Surf. Sci. Catal.*, 2000, **130 B**, 1847–1852.
- 14 E. Heracleous and A. A. Lemonidou, *J. Catal.*, 2010, 270, 67–75.
- 15 R. Farhi and G. Petot-Ervas, J. Phys. Chem. Solids, 1978, 39, 1169-1173.
- 16 T. Chen, W. Li, C. Yu, R. Jin and H. Xu, Stud. Surf. Sci. Catal., 2000, 130, 1847–1852.
- 17 E. Heracleous and A. A. Lemonidou, J. Catal., 2006, 237, 162–174.
- 18 E. Heracleous and A. A. Lemonidou, *J. Catal.*, 2006, 237, 175–189.
- 19 Z. Skoufa, E. Heracleous and A. A. Lemonidou, J. Catal., 2015, 322, 118-129.
- 20 J. L. Park, S. K. Balijepalli, M. D. Argyle and K. J. Stowers, *Ind. Eng. Chem. Res.*, 2018, 57, 5234–5240.
- 21 B. Solsona, P. Concepción, S. Hernández, B. Demicol and J. M. L. Nieto, *Catal. Today*, 2012, **180**, 51–58.
- 22 B. Solsona, J. M. López Nieto, P. Concepción, A. Dejoz, F. Ivars and M. I. Vázquez, J. Catal., 2011, 280, 28–39.
- 23 H. Zhu, D. C. Rosenfeld, M. Harb, D. H. Anjum, M. N. Hedhili, S. Ould-Chikh and J. M. Basset, *ACS Catal.*, 2016, 6, 2852–2866.
- 24 Z. Skoufa, G. Xantri, E. Heracleous and A. A. Lemonidou, *Appl. Catal.*, *A*, 2014, **471**, 107–117.
- 25 D. Delgado, B. Solsona, A. Ykrelef, A. Rodríguez-Gómez, A. Caballero, E. Rodríguez-Aguado, E. Rodríguez-Castellón and J. M. López Nieto, *J. Phys. Chem. C*, 2017, **121**, 25132–25142.
- 26 B. Solsona, P. Concepción, B. Demicol, S. Hernández, J. J. Delgado, J. J. Calvino and J. M. López Nieto, *J. Catal.*, 2012, 295, 104–114.

- 27 A. M. Turky, Appl. Catal., A, 2003, 247, 83-93.
- 28 M. Capdevila-Cortada, M. García-Melchor and N. López, J. Catal., 2015, 327, 58–64.
- 29 Z. A. Qiao, Z. Wu and S. Dai, *ChemSusChem*, 2013, 6, 1821-1833.
- 30 Q. Hua, T. Cao, X.-K. Gu, J. Lu, Z. Jiang, X. Pan, L. Luo, W.-X. Li and W. Huang, *Angew. Chem.*, 2014, **126**, 4956–4961.
- 31 E. E. Platero, G. S. Coluccia and A. Zecchina, *Langmuir*, 1987, 3, 291–297.
- 32 G. A. El-Shobaky, I. F. Hewaidy and T. H. El-Nabarawi, Surf. Technol., 1981, 12, 309–315.
- 33 X. Xu, L. Li, J. Huang, H. Jin, X. Fang, W. Liu, N. Zhang, H. Wang and X. Wang, ACS Catal., 2018, 8, 8033–8045.
- 34 H. Zhu, H. Dong, P. Laveille, Y. Saih, V. Caps and J. M. Basset, *Catal. Today*, 2014, 228, 58–64.
- 35 Q. Ren, Z. Feng, S. Mo, C. Huang, S. Li, W. Zhang, L. Chen, M. Fu, J. Wu and D. Ye, *Catal. Today*, 2018, 332, 160–167.
- 36 H. X. Mai, L. D. Sun, Y. W. Zhang, R. Si, W. Feng, H. P. Zhang, H. C. Liu and C. H. Yan, *J. Phys. Chem. B*, 2005, 109, 24380–24385.
- 37 E. Aneggi, D. Wiater, C. De Leitenburg, J. Llorca and A. Trovarelli, *ACS Catal.*, 2014, 4, 172–181.
- 38 Y. Kwon, A. Soon, H. Han and H. Lee, *J. Mater. Chem. A*, 2015, 3, 156–162.
- 39 Y. Xu, H. Wang, Y. Yu, L. Tian, W. Zhao and B. Zhang, J. Phys. Chem. C, 2011, 115, 15288–15296.
- 40 M. D. Susman, H. N. Pham, X. Zhao, D. H. West, S. Chinta, P. Bollini, A. K. Datye and J. D. Rimer, *Angew. Chem., Int. Ed.*, 2020, **59**, 15119.
- 41 M. D. Susman, H. N. Pham, A. K. Datye, S. Chinta and J. D. Rimer, *Chem. Mater.*, 2018, **30**, 2641–2650.
- 42 P. M. Oliver, G. W. Watson and S. C. Parker, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1995, **52**, 5323–5329.
- 43 P. M. Oliver, S. C. Parker and W. C. Mackrodt, *Modell. Simul. Mater. Sci. Eng.*, 1993, 1, 755–760.
- 44 F. Lin, D. Nordlund, T. C. Weng, D. Sokaras, K. M. Jones, R. B. Reed, D. T. Gillaspie, D. G. J. Weir, R. G. Moore, A. C. Dillon, R. M. Richards and C. Engtrakul, *ACS Appl. Mater. Interfaces*, 2013, 5, 3643–3649.
- 45 C. M. Lampert, T. R. Omstead and P. C. Yu, *Sol. Energy Mater.*, 1986, 14, 161–174.
- 46 G. A. Niklasson and C. G. Granqvist, J. Mater. Chem., 2007, 17, 127–156.
- 47 J. Haber and F. S. Stone, Trans. Faraday Soc., 1963, 59, 192.
- 48 F. P. Larkins and P. J. Fensham, *Trans. Faraday Soc.*, 1970, **66**, 1755–1772.
- 49 S. J. Teichner and J. A. Morrison, *Trans. Faraday Soc.*, 1955, **51**, 961–966.
- 50 K. Klier, Catal. Rev., 1968, 1, 207-232.
- 51 C. Dong, Z. Qu, Y. Qin, Q. Fu, H. Sun and X. Duan, ACS Catal., 2019, 9, 6698–6710.
- 52 S. Anke, G. Bendt, I. Sinev, H. Hajiyani, H. Antoni, I. Zegkinoglou, H. Jeon, R. Pentcheva, B. R. Cuenya, S. Schulz and M. Muhler, ACS Catal., 2019, 9, 5974–5985.
- 53 Y. Zheng, S. Thampy, N. Ashburn, S. Dillon, L. Wang, Y. Jangjou, K. Tan, F. Kong, Y. Nie, M. J. Kim, W. S. Epling, Y. J.

Chabal, J. W. P. Hsu and K. Cho, *J. Am. Chem. Soc.*, 2019, **141**, 10722–10728.

- 54 M. Iwamoto, Y. Yoda, M. Egashira and T. Seiyama, J. Phys. Chem., 1976, 80, 1989–1994.
- 55 M. Iwamoto, Y. Yoda, N. Yamazoe and T. Seiyama, *J. Phys. Chem.*, 1978, **82**, 2564–2570.
- 56 Y. Wu, Y. He, T. Wu, W. Weng and H. Wan, *Mater. Lett.*, 2007, **61**, 2679–2682.
- 57 Z. Skoufa, E. Heracleous and A. A. Lemonidou, *Catal. Today*, 2012, **192**, 169–176.
- 58 N. Ashburn, Y. Zheng, S. Thampy, S. Dillon, Y. J. Chabal, J. W. P. Hsu and K. Cho, *ACS Appl. Mater. Interfaces*, 2019, **11**, 30460–30469.
- 59 J. L. Brito, J. Laine and K. C. Pratt, J. Mater. Sci., 1989, 24, 425–431.
- 60 V. C. F. Holm and A. Clark, J. Catal., 1968, 11, 305–316.
- 61 J. A. Rodriguez, J. C. Hanson, A. I. Frenkel, J. Y. Kim and M. Pérez, J. Am. Chem. Soc., 2002, **124**, 346–354.
- 62 N. K. Kotsev and L. I. Ilieva, Catal. Lett., 1993, 18, 173-176.
- 63 K. Chen, A. Khodakov, J. Yang, A. T. Bell and E. Iglesia, J. Catal., 1999, 186333, 325–333.
- 64 X. Li and E. Iglesia, J. Phys. Chem. C, 2008, 112, 15001–15008.
- 65 H. Zhu, S. Ould-Chikh, D. H. Anjum, M. Sun, G. Biausque, J. M. Basset and V. Caps, *J. Catal.*, 2012, 285, 292–303.

- 66 B. Savova, S. Loridant, D. Filkova and J. M. M. Millet, *Appl. Catal.*, A, 2010, **390**, 148–157.
- 67 V. Fleischer, R. Steuer, S. Parishan and R. Schomäcker, J. Catal., 2016, 341, 91–103.
- 68 G. I. Panov, K. A. Dubkov and E. V. Starokon, *Catal. Today*, 2006, **117**, 148–155.
- 69 K. Aika and J. H. Lunsford, J. Phys. Chem., 1978, 82, 1794–1800.
- 70 E. Morales and J. H. Lunsford, J. Catal., 1989, 118, 255-265.
- 71 K. Aika and J. H. Lunsford, *J. Phys. Chem.*, 1977, **81**, 1393–1398.
- 72 M. B. Ward, M. J. Lin and J. H. Lunsford, J. Catal., 1977, 50, 306–318.
- 73 X. Lin, Y. Xi and J. Sun, J. Phys. Chem. C, 2012, 116, 3503-3516.
- 74 J. J. Varghese and S. H. Mushrif, J. Phys. Chem. C, 2017, 121, 17969–17981.
- 75 Y.-F. Y. Yao and J. T. Kummer, J. Catal., 1973, 28, 124–138.
- 76 S. T. Oyama, A. M. Middlebrook and G. A. Somorjai, J. Phys. Chem., 1990, 94, 5029–5033.
- 77 M. D. Argyle, K. Chen, A. T. Bell and E. Iglesia, J. Phys. Chem. B, 2002, 106, 5421–5427.
- 78 K. Chen, A. T. Bell and E. Iglesia, J. Phys. Chem. B, 2000, 104, 1292–1299.