Reactivity and stability investigation of supported molybdenum oxide catalysts for the hydrodeoxygenation (HDO) of m-cresol

Manish Shetty¹, Karthick Murugappan ¹, Teerawit Prasomsri, William H. Green, Yuriy Román-Leshkov *

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

A R T I C L E   I N F O

Article history:
Received 19 May 2015
Revised 25 July 2015
Accepted 31 July 2015
Available online 15 September 2015

This article is dedicated to Prof. Jean-Pierre Gilson on the occasion of his birthday. His seminal work in the areas of adsorption, catalysis, zeolite chemistry, and biomass conversion inspired us to undertake the present line of research involving reducible metal oxides for the deoxygenation of biomass-derived molecules. We wholeheartedly congratulate Jean-Pierre, wishing him continuing success in his work.

Keywords:
Hydrodeoxygenation (HDO)
Lignin-derived oxygenates
m-Cresol
Supported molybdenum oxides
Metal–support interaction
Biomass conversion

A B S T R A C T

The vapor-phase hydrodeoxygenation (HDO) of m-cresol is investigated at 593 K and H₂ pressures < 1 bar for supported catalysts comprised of 10 wt% MoO₃ dispersed over SiO₂, γ-Al₂O₃, TiO₂, ZrO₂, and CeO₂. Reactivity data show that all catalysts selectively cleave C–O bonds without saturating the aromatic ring, thus effectively transforming m-cresol into toluene at moderate to high conversions. MoO₃/ZrO₂ and MoO₃/TiO₂ feature the highest initial site time yields (23.4 and 13.9 h⁻¹, respectively) and lowest first-order deactivation rate constants (0.013 and 0.006 h⁻¹, respectively) of all catalysts tested after ca. 100 h on stream. Characterization studies demonstrate that the supports play an important role in stabilizing partially reduced, coordinatively unsaturated (CU) sites in surface oligomeric Mo moieties. Post-reaction X-ray photoelectron spectroscopy shows that the catalysts with higher activity feature larger proportions of intermediate oxidation species (Mo⁵⁺ and Mo³⁺). In contrast, the catalysts with lower reactivity show different oxidation states: bulk MoO₃ features mostly Mo⁴⁺ and metallic Mo species, while MoO₃/CeO₂ features a high proportion of Mo⁶⁺ species. An inverse correlation is established between the catalyst activity and both the maximum hydrogen consumption temperature obtained during temperature programmed reduction, and the support cation electronegativity (with the exception of MoO₃/CeO₂).

1. Introduction

Catalytic fast pyrolysis (CFP) is an attractive technology to convert biomass into fuel additives and value-added chemicals [1–4]. Zeolites have recently been shown to be highly effective catalysts for converting lignocellulosic biomass to gasoline-range aromatics via CFP [5–7]. However, given that lignocellulosic biomass is inherently hydrogen poor with a H/Cₐₑff ratio (defined as [(H – 2O)/C]) ranging from 0 to 0.3, the maximum yield of hydrocarbons that can be obtained by upgrading it in the absence of external H₂ is severely limited by stoichiometry. As such, upgrading with zeolites typically results in aromatic and olefinic hydrocarbon yields near 30% concomitant with high coke formation [5,8]. Conventional hydrotreating catalysts (e.g., sulfided CoMo and NiMo) and supported noble metal catalysts have been reported to produce stable and energy dense products from pyrolysis oils [2,9–12]. However, they require high H₂ pressures that lead to aromatic ring hydrogenation, resulting in reduced octane number and increased H₂ consumption [2]. In light of these challenges, it is desirable to develop technologies that use H₂ to selectively cleave C–O bonds without aromatic ring saturation, at preferably low H₂ pressures.

Recently, Román-Leshkov and coworkers demonstrated that several reducible metal oxides, including MoO₃, are effective hydrodeoxygenation (HDO) catalysts capable of selectively cleaving C–O bonds in various bio-derived oxygenates to produce olefinic and aromatic hydrocarbons. Remarkably, the HDO reactions were catalyzed at mild conditions of 593 K and H₂ partial pressures < 1 bar [13,14]. It was hypothesized that HDO occurs via an oxygen vacancy driven mechanism over a partially carburized molybdenum surface. The characterization data showed that Mo⁵⁺ species were important for maintaining HDO activity, and suggested that the phase transformation of MoO₃ to an oxytocarbonydride (MoO₃C₂H₆) played a critical role in stabilizing these Mo⁵⁺ species by preventing the over-reduction to less active Mo⁶⁺ species [14–16].
High surface area supports are ubiquitously used to increase the
dispersion of active Mo species [17–19]. Importantly, some supports
have been shown to drastically influence the catalytic activity
of Mo species by stabilizing specific oxidation states [20], or by
influencing the geometric configurations [21], electronic properties
[22], and prevalence of “high-energy” sites [23]. For instance, the
nature of the Mo–O–support bond in surface MoO₃ domains was
shown to influence catalytic activity during the oxidative dehydro-
genation of alkanes, as well as other oxidation reactions [24–28].

Notably, the increase in the steady-state turn-over frequency
(TOF) was observed to inversely correlate with the support cation
electronegativity [24,27]. Recently, ZrO₂, CeO₂, and TiO₂ have been
studied as supports for the HDO of lignin-derived model com-
 pounds using CoMoS, MoS₂, Ni, and Cu–Ni–based catalysts
[12,29–31]. To date, however, no comprehensive studies have been
performed on supported MoO₃ catalysts for HDO.

In this work, we investigate the influence of supports, including
SiO₂, γ-Al₂O₃, TiO₂, ZrO₂, and CeO₂, on the reactivity and stability of
dispersed MoO₃ during the hydrodeoxygenation of m-cresol—a
model bio-oil compound. Supported catalysts are synthesized with
cia. 10 wt% MoO₃ loading, which corresponds to near-monolayer
oligomeric MoO₃ species on the support surface. Reactivity studies
are performed to identify differences in activity that arise from
specific Mo-support interactions. Oxygen chemisorption is used
to determine the number of redox-active Mo sites, and initial site
time yields (STYs) are then used to compare the performance of dif-
f erent catalysts. Reactivity data are then combined with detailed
catalytic characterization techniques to identify the genesis of the observed
reactivity differences. Post-reaction analysis with X-ray photoelec-
tron spectroscopy (XPS) and temperature programmed oxidation-
mass spectrometry (TPO-MS) provide insights on the preferential
stabilization of specific Mo oxidation states by each support, as well as
overall propensity for coking. These data are then correlated to
long-term stability and regenerability properties of the catalyst.

2. Experimental

2.1. Catalyst materials and synthesis

The feed, m-cresol (99%, Sigma–Aldrich), was used without fur-
ther purification. H₂ (99.999%), He (99.999%), O₂ (99.999%) and air
(dry grade, Airgas) were purchased from Airgas. Molybdenum (VI)
oxide (MoO₃ > 99.5 wt%), molybdenum (IV) oxide (MoO₂ > 99 wt
%), and molybdenum carbide (Mo₂C > 99 wt%) were purchased from Sigma–Aldrich. α-Alumina oxide, α-Al₂O₃ (100–200 mesh,
> 99 wt%), Sigma–Aldrich) was used as an inert diluent for all reac-
tions. Titanium (IV) oxide, TiO₂ (majority anatase, 21 nm, > 99.5 wt
%), and silicon oxide, SiO₂ (5–15 nm, 99.5 wt%) were purchased from Sigma–Aldrich and used directly as supports. γ-Alumina oxide
(γ-Al₂O₃, 0.3175 cm pellets, Alfa Aesar) was ground and sieved with
a 200 mesh (<74 μm) for use as support. Zirconium (IV) oxide (ZrO₂) and cerium (IV) oxide (CeO₂) nanoparticles were
synthesized using previously reported methods [32].

Supported 10 wt% MoO₃ catalysts were prepared using wet
impregnation method. For a batch of 5 g of supported catalyst, 5 ml aqueous solution of 0.614 g ammonium paramolybdate tetra
(paraoxalate) (NH₄)₂MoO₃·4H₂O, 99%, Alfa Aesar) was added dropwise to the support (4.5 g) under vigorous stirring. The sample
was then dried at 373 K for 12 h and calcined at 823 K (ramp rate
10 K min⁻¹) in air at a flow rate of 100 ml min⁻¹ for 3 h. Bulk MoO₃
was activated under identical conditions.

2.2. Catalyst activity measurement and product analysis

Catalytic activity and stability experiments were carried out in a
vapor-phase packed-bed down-flow reactor. The reactor consisted
of a stainless-steel tube (0.95 cm OD) with wall thickness
(0.089 cm) mounted in a single-zone furnace (Applied Test Sys-
tems, Series 3210, 850W/115V). The temperature was controlled
by a temperature controller (Digi-Sense, model 68900-10) con-
ected to a K-type thermocouple (Omega, model TJJ36-CAXL-
116u) mounted downstream in direct contact with the catalyst
bed. The catalyst was mixed with γ-Al₂O₃ (total 1 g) and packed
between two inert layers of γ-Al₂O₃ (1.5 g each) and kept in
the middle of the furnace. The total volume of the bed was approxi-
mately 2 cm³. Prior to reaction, the reactor temperature was
ramped at a rate of 6 K min⁻¹ under He to the reaction temperature
of 593 K. Next, m-cresol was delivered into the reactor via a capil-
lary tube connected to a syringe pump (Harvard Apparatus, model
703005) and mixed with H₂ gas at the inlet of the reactor. Flow
rates were adjusted to obtain weight hourly space velocity (WHSV)
values of 8.27 h⁻¹.

\[
\text{WHSV (h}^{-1}) = \frac{\text{mass flow rate of reactant fed}}{\text{mass of equivalent MoO}_3 \text{ loaded}}
\]

(1)

The reactor effluent lines were heated to 523 K to prevent any
condensation of effluents. The effluents were analyzed and quanti-
fied via an online gas chromatograph (GC) equipped with a mass
selective detector for identification (MSD, Agilent Technologies,
model 5975 C) and a flame ionization detector for quantification
(FID, Agilent Technologies, model 7890 A). The GC was fitted with
a DB-5 column (Agilent, 30 m × 0.25 mm ID × 0.25 μm). The GC
parameters used for analysis are as follows: detector temperature
573 K, injector temperature 548 K, split ratio 1:20. The initial and
final oven temperatures were 343, and 473 K, with a ramp of
8 K min⁻¹.

The following definitions were used to quantify experimental
data:

\[
\text{Conversion (\%) =} \frac{\text{moles of carbon of reactant consumed}}{\text{moles of carbon of reactant fed}} \times 100
\]

(2)

\[
\text{Rate of conversion (mmol h}^{-1} \text{ g}^{-1} \text{MoO}_3) = \frac{\text{molar flow rate of reactant consumed}}{\text{mass of equivalent MoO}_3 \text{ loaded}}
\]

(3)

\[
\text{Selectivity to hydrocarbons (\%) =} \frac{\text{moles of carbon of hydrocarbons in product}}{\text{moles of carbon of reactant consumed}} \times 100
\]

(4)

\[
\text{Yield (\%) =} \frac{\text{moles of carbon of product}}{\text{moles of carbon of reactant fed}} \times 100
\]

(5)

The reaction was run in the absence of external and internal
mass-transfer limitations (Supporting Information). For most cata-
lysts, initial reactivity data were obtained by operating at low con-
versions (<14%). The initial rates for MoO₃/TiO₂ and MoO₃/ZrO₂
were estimated from high-conversion data, after establishing a
zero-order dependence with respect to the oxygenate concentra-
tion (Fig. S1, Supporting Information). The catalyst deactivation
rate constants were obtained by fitting deactivation profiles to a
first-order deactivation model, as reported previously [13,14,33].

2.3. Catalyst characterization

All pre-reaction catalyst characterizations were carried out on
calcined samples. Powder X-ray diffraction (PXRD) patterns were
collected using a Bruker D8 diffractometer with Nickel-filtered
Cu Kα radiation (λ = 1.5418 Å). Diffraction data were recorded on a
2D image plate rotated at a speed of 15 rpm, between 2θ values of
20–90° and a total scan time of 30 min. The diffraction patterns
were normalized to maximum peak intensity for each catalyst. Raman spectroscopy was performed on a HORIBA Jobin Yvon using a 532 nm laser with a maximum power of 100 mW, and at an optical magnification of 50×. The spectra were collected from Raman shifts between 200 and 1200 cm⁻¹ and were normalized to the maximum peak intensity for each catalyst. The spectra between 750 and 1050 cm⁻¹ were similarly normalized to study the dispersion of Mo species on the surface of the support. Diffuse reflectance UV–Vis spectra were recorded on a Cary 5000 (Varian) instrument equipped with a Praying Mantis diffuse reflectance accessory (Harrick Scientific Products) using BaSO₄ (Sigma–Aldrich, 99%) as a white reference. Reflectance was converted to absorbance using the Kubelka–Munk function $F(R_s)$. The absorption-edge energy was calculated using the $x$-intercept of the straight line fitted through low energy rise of spectra, $F(R_s)hv^2$ plotted as a function of $hv$, where $h$ is the energy of an incident photon, as previously reported [34].

Surface area measurements and oxygen chemisorption experiments were carried out on Quantachrome Autosorb IQ automated gas sorption system. The surface area was determined using nitrogen adsorption–desorption experiments at a liquid nitrogen temperature (77 K) using the Brunauer–Emmett–Teller (BET) theory. The surface area was determined using nitrogen gas (Airgas) at a total flow rate of 20 ml min⁻¹. The temperature was equilibrated at 303 K and ramped at 7.5 K min⁻¹ to 923 K. The CO₂ ($m/z = 44$) and Ar ($m/z = 40$) signals (internal standard) were monitored using the MS. The amount of carbonaceous species was quantified by calculating the evolved CO₂ against a calibration curve prepared using graphite standard (powder, <20 μm, synthetic, Sigma–Aldrich).

XPS was performed using a PHI Versaprobe II instrument equipped with a multi-channel hemispherical analyser and an aluminium anode X-ray source operating at 100 W, featuring a 100 μm beam scanned over a 1.4 mm line across the sample surface. A dual-beam charge neutralization system was used with an electron neutralizer bias of 1.2 eV and an Ar ion beam energy of 10 eV. Except for long TOS runs (~100 h), all post-reaction catalysts samples used for XPS analysis were prepared under identical conditions to those used for reactivity measurements, but were not mixed with the α-Al₂O₃ diluent to allow for easy recovery. Samples were passivated in a stream of 1% O₂, balance N₂ (Airgas) gas mixture at a flow rate of 100 ml min⁻¹, and a temperature below 303 K for 1 h after reaction. The catalysts were recovered and immediately moved to glove box for storage in Ar atmosphere prior to analysis. These post-reaction samples were mixed with niobium oxide (Nb₂O₅, 99.99%, Sigma Aldrich) as an internal standard for charge correction. The binding energies were corrected to 207.4 eV (Nb 3d₅/₂). In the case of long TOS runs, binding energies were corrected to 208.4 eV (C 1s), 182.3 eV (Zr 3d₅/₂), 458.5 eV (Ti 2p₃/₅) for bulk MoO₃, MoO₃·ZrO₂, and MoO₃/TiO₂, respectively, as the addition of Nb₂O₅ would have led to a low signal-to-noise ratio. A 7-point Shirley background correction was then applied to the Mo 3d XPS spectra after charge correction. The composition of Mo oxidation states was estimated by the deconvolution of Mo 3d spectra. The following constraints were used for deconvolution: (1) Splitting energy of 3.15 eV for Mo 3d₅/₂–Mo 3d₃/₂, (2) Area intensity ratio of 3:2 for Mo 3d₅/₂–Mo 3d₃/₂, and (3) Equal full width at half maximum (FWHM) of Mo 3d₅/₂ and Mo 3d₃/₂.

Mo loading on the support was determined from elemental analysis using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Activa-S, HORIBA Scientific). Samples were dissolved in a 1:1 mixture of 48% hydrogen fluoride, (HF, Sigma–Aldrich) and reagent grade nitric acid (HNO₃, Sigma–Aldrich). The solution was then dispersed in 2% HNO₃ before analysis. A 4-point calibration curve was built using dilutions of a 1000 ppm Mo standard. The Mo spectral line at 202.03 nm was used for the ICP-AES analysis.

3. Results

3.1. Pre-reaction catalyst characterization

ICP-AES analysis confirmed the MoO₃ loading on the supported catalysts to be within 1% of the theoretical loading of 10 wt%. Powder X-ray diffraction (PXRD) patterns for the bare supports and the supported catalysts are shown in Fig. 1 and Fig. S2 (Supporting Information). With the exception of MoO₃/TiO₂, no differences

\[
\text{Moles of redox active Mo species} = 2 \times \frac{\text{oxygen uptake in mol g}^{-1} \times \text{catalyst mass in g}}{\text{Mo loading in mol g}^{-1} \times 100}
\]

\[
\text{Redox active Mo species (\%)} = 2 \times \frac{\text{oxygen uptake in mol g}^{-1}}{\text{Mo loading in mol g}^{-1}} \times 100
\]

\[
\text{Areal rate of conversion (\mu mol h}^{-1} \text{m}^{-2}) = \frac{\text{Rate of conversion}}{\text{BET surface area of catalyst}}
\]

\[
\text{Site time yield (h}^{-1}) = \frac{\text{molar flow rate of HDO product (toluene) formed}}{\text{moles of redox active Mo species}}
\]

\[
\text{Temperature programmed reduction (TPR) was performed in a quartz U-tube setup connected to a mass spectrometer (MS, Hiden Analytical HPR-20/QIC). A quartz U-tube was loaded with a bed of either supported catalyst (400 mg), or support (360 mg). The catalyst bed was in contact with a K-type thermocouple (Omega, model TJ36-CAXL-116u), which was connected to a temperature controller (Digi-Sense, model 688900-10). The U-tube was placed in a furnace (Carbolite®, model GTF 11/50/750B, 575W/115 V) connected to the temperature controller. Samples were calcined in O₂ (100 ml min⁻¹) at 773 K for 2 h (ramp rate 8.3 K min⁻¹) and cooled under Ar (high purity, Airgas) to room temperature. The temperature was then increased to 873 K at a ramp rate of 2 K min⁻¹ under a gas mixture of 1% H₂, 1% Ar, and balance He, at a total flow rate of 50 ml min⁻¹. The evolution of H₂O (m/z = 18), consumption of H₂ (m/z = 2), and the Ar (m/z = 40) signal were tracked using MS, where Ar was used as an internal standard. The temperature corresponding to the peak consumption of H₂ is referred to as the temperature of maximum consumption (Tmax).

The nature and quantity of deposited carbon species on post-reaction catalysts were analyzed by TPO-MS, using a thermogravimetric analyzer (TGA, TA Instruments TGA-Q500) combined with a mass spectrometer (MS, Hiden Analytical HPR-20/QIC). A gas mixture of 1% O₂, 1% Ar, and balance He (Airgas) was used at a total flow rate of 20 ml min⁻¹. The temperature was equilibrated at 303 K and ramped at 7.5 K min⁻¹ to 923 K. The CO₂ (m/z = 44) and Ar (m/z = 40) signals (internal standard) were monitored using the MS. The amount of carbonaceous species was quantified by calculating the evolved CO₂ against a calibration curve prepared using a graphite standard (powder, <20 μm, synthetic, Sigma–Aldrich).

XPS was performed using a PHI Versaprobe II instrument equipped with a multi-channel hemispherical analyser and an aluminium anode X-ray source operating at 100 W, featuring a 100 μm beam scanned over a 1.4 mm line across the sample surface. A dual-beam charge neutralization system was used with an electron neutralizer bias of 1.2 eV and an Ar ion beam energy of 10 eV. Except for long TOS runs (~100 h), all post-reaction catalyst samples used for XPS analysis were prepared under identical conditions to those used for reactivity measurements, but were not mixed with the α-Al₂O₃ diluent to allow for easy recovery. Samples were passivated in a stream of 1% O₂, balance N₂ (Airgas) gas mixture at a flow rate of 100 ml min⁻¹, and a temperature below 303 K for 1 h after reaction. The catalysts were recovered and immediately moved to glove box for storage in Ar atmosphere prior to analysis. These post-reaction samples were mixed with niobium oxide (Nb₂O₅, 99.99%, Sigma Aldrich) as an internal standard for charge correction. The binding energies were corrected to 207.4 eV (Nb 3d₅/₂). In the case of long TOS runs, binding energies were corrected to 208.4 eV (C 1s), 182.3 eV (Zr 3d₅/₂), 458.5 eV (Ti 2p₃/₅) for bulk MoO₃, MoO₃·ZrO₂, and MoO₃/TiO₂, respectively, as the addition of Nb₂O₅ would have led to a low signal-to-noise ratio. A 7-point Shirley background correction was then applied to the Mo 3d XPS spectra after charge correction. The composition of Mo oxidation states was estimated by the deconvolution of Mo 3d spectra. The following constraints were used for deconvolution: (1) Splitting energy of 3.15 eV for Mo 3d₅/₂–Mo 3d₃/₂, (2) Area intensity ratio of 3:2 for Mo 3d₅/₂–Mo 3d₃/₂, and (3) Equal full width at half maximum (FWHM) of Mo 3d₅/₂ and Mo 3d₃/₂.

Mo loading on the support was determined from elemental analysis using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Activa-S, HORIBA Scientific). Samples were dissolved in a 1:1 mixture of 48% hydrogen fluoride, (HF, Sigma–Aldrich) and reagent grade nitric acid (HNO₃, Sigma–Aldrich). The solution was then dispersed in 2% HNO₃ before analysis. A 4-point calibration curve was built using dilutions of a 1000 ppm Mo standard. The Mo spectral line at 202.03 nm was used for the ICP-AES analysis.
were observed between each set of diffractograms, indicating that there was no change in the topology of support after dispersion of the Mo species. MoO₃/TiO₂ shows the presence of MoO₃ peaks at 2θ = 23.7°, and 34.2°, indicating the formation of crystalline MoO₃ clusters. In general, these data suggest that MoO₃ is well dispersed on the support surface. However, we cannot rule out the presence of clusters smaller than the PXRD crystallite size limits of ~4 nm. Raman spectroscopy was used to detect any local changes within dispersed molybdenum oxide domains by probing Mo–O vibrational modes of all supported catalysts (Fig. 2 (a) and (b)). Specifically, the ν_{asymmetric} (Mo–O–Mo) and terminal ν (Mo=O) stretching modes provide information on the local structure of dispersed MoO₃ domains. In agreement with the PXRD results, of all catalysts tested, only MoO₃/TiO₂ shows bands at 820, and 995 cm⁻¹ corresponding to crystalline MoO₃. However, these band intensities are lower than those seen for ν (Mo=O) at ca. 980 cm⁻¹, which correspond to oligomeric octahedral Mo species [36]. Crystalline MoO₃ bands are 10–10³ times more intense than both isolated and oligomeric species [37,38]. Hence, the relatively weak intensity of crystalline MoO₃ bands suggests that oligomeric MoO₃ domains are predominant on these catalysts. Further, the absence of bands at 745 and 1000 cm⁻¹ for MoO₃/ZrO₂; 822, 890, and 915 cm⁻¹ for MoO₃/γ-Al₂O₃; and 320, 380, 910, and 955 cm⁻¹ for MoO₃/γ-Al₂O₃ indicates that crystalline heterometallic molybdates, such as Zr(MoO₄)₂, Al₂(MoO₄)₃, and Ce₂Mo₄O₁₅, are not formed on the catalyst surface [39–42]. MoO₃/ZrO₂ has bands at ca. 810, 865, 950, and 980 cm⁻¹. The latter two have been assigned to ν (Mo=O) for oligomeric MoO₃ domains [38,40]. The bands at ca. 810 and 865 cm⁻¹ have been assigned to either oligomeric ν_{asymmetric} (Mo–O–Mo) and/or ν_{asymmetric} (Mo–O–Zr) [40]. The presence of two bands for ν (Mo=O) may also suggest the existence of two different species that were not observed for other supported catalysts. Similarly, the ν_{asymmetric} (Mo–O–Mo) band at ca. 220 cm⁻¹ for both MoO₃/γ-Al₂O₃ and MoO₃/γ-Al₂O₃, the ν_{stretching} (Mo–O–Mo) band at ca. 340 and 380 cm⁻¹ for MoO₃/γ-Al₂O₃, and MoO₃/γ-Al₂O₃, respectively, and the ν (Mo=O) band at ca. 950 cm⁻¹ for both MoO₃/γ-Al₂O₃ and MoO₃/γ-Al₂O₃, can all be attributed to oligomeric MoO₃ domains. The presence of ν (Mo=O) bands at ca. 940 and 990 cm⁻¹ (dehydrated) for MoO₃/γ-Al₂O₃ and ν_{asymmetric} (Mo–O–Mo) bands at ca. 880, and 800 cm⁻¹ for MoO₃/γ-Al₂O₃, and MoO₃/γ-Al₂O₃, respectively, further confirm the oligomeric nature of MoO₃ domains [26,41,43–51]. Taken together, the PXRD and Raman spectroscopy data indicate that at loadings of 10 wt%, the MoO₃ domains are dispersed on the support surface mostly as oligomeric species, regardless of the support used.

3.2. Catalyst physical properties and redox-active site quantification

Physical properties of the supports and supported Mo catalysts used in this study, including surface area, oxygen uptake, and percentage of redox-active Mo species are summarized in Table 1. With the exception of MoO₃/TiO₂, the surface area of all catalysts reduced upon incorporation of dispersed Mo species on the support. The reduction in surface area may be attributed to the blockage of pores by larger MoO₃ domains [52,53]. The negligible change in surface area for TiO₂ upon dispersion of Mo species has also been reported by Tsilomelekis et al. [27]. MoO₃/γ-Al₂O₃ showed the largest reduction in surface area from 83.4 to 29.7 m²/g (64.4%), which is also consistent with previous reports [54].

Oxygen chemisorption data show that MoO₃/TiO₂ featured the highest oxygen uptake values (245.0 μmol/g), followed by MoO₃/ZrO₂ (137.9 μmol/g), and MoO₃/γ-Al₂O₃ (131.0 μmol/g). MoO₃/γ-Al₂O₃ and MoO₃/γ-Al₂O₃ had much lower oxygen uptake values of 98.3 and 43.1 μmol/g, respectively. Desikan et al. used oxygen uptake values to quantify the number of redox-active Mo species on the support surface, which differ based on the nature of interaction between Mo and support [55]. Reduction and chemisorption temperature of 623 K was used for all supported MoO₃ catalysts in accordance with the literature reports for quantifying O₂ uptake on MoO₃/SiO₂, MoO₃/TiO₂, MoO₃/γ-Al₂O₃, and MoO₃/γ-Al₂O₃ [52,53,55–57]. We note that the 623 K temperature used for reduction is close to 593 K used in our reactivity studies. The oxygen uptake values were used to determine the number of redox-active Mo species, allowing us to normalize HDO reactivity for all supported catalysts.

3.3. H₂-temperature programmed reduction (TPR) of supported MoO₃ catalysts

Reducibility of supported catalysts was investigated by TPR (see Fig. 3). Control experiments of the bare supports show that, with the exception of CeO₂, the supports do not show any appreciable H₂ consumption in the range of 573–873 K (Fig. S3, Supporting Information). Therefore, the observed maximum temperature of hydrogen consumption (T_max) for the supported catalysts can be attributed to the reduction of dispersed octahedral Mo⁶⁺ species to lower oxidation states [58]. MoO₃(ZrO₂, MoO₃/TiO₂, and MoO₃/γ-Al₂O₃ featured significantly lower T_max values of ca. 680, 710, and 685 K, respectively. Further, MoO₃/ZrO₂ has an additional peak at ca. 725 K. This peak may suggest the presence of two different Mo species, in agreement with the two bands for ν (Mo=O) observed in the Raman spectrum (Fig. 2(b)). On the other hand, MoO₃/SiO₂ and MoO₃/γ-Al₂O₃ show higher T_max values of ca. 790 and 810 K, respectively. The T_max values for all catalysts agree well with the literature values reported for the similar loadings of MoO₃ on these supports [36,48,57–59]. Bulk MoO₃ has T_max values at 995, 1050, and 1090 K (Fig. S4, Supporting Information), with first two peaks corresponding to the reduction of MoO₃ to Mo₂O₅, and the minor last peak corresponding to conversion of MoO₃ to Mo₃O₈ [57,60]. This progression is consistent with previous studies showing the formation of MoO₂ before Mo₃O₈ [61]. These T_max values are considerably higher than those observed for the supported catalysts as they correspond to bulk phase transformations [52].

3.4. Diffuse reflectance UV–Visible (DR UV–Vis) spectroscopy

The local structure of Mo (VI) species was probed with UV–Vis spectroscopy, focusing on ligand-to-metal charge transfer (LMCT) transitions (Figs. S5 and S6, Supporting Information) and their corresponding absorption-edge energies (Eₘ) (Table 2). From the five supports used in the study, ZrO₂, TiO₂, and CeO₂ absorb strongly
in the UV–Vis region in decreasing order of absorption-edge energies (Table 2), and overlap with LMCT transitions for Mo (VI) species ($O_2$/$C_0$) for Mo$_6^+$) in the wavelength range of 200–600 nm (Fig. S5 (a)) [62]. Both SiO$_2$ and cAl$_2$O$_3$ are weak absorbers in the UV–Vis region, and their absorption can therefore be neglected (Fig. S5 (b)). Although bands corresponding to LMCT transitions of supported molybdenum (VI) species are broad and do not provide definite structural information [44], recent studies have used the absorption-edge energies of these LMCT transitions to provide quantitative information on the local structures of Mo (VI) species [34,51,63]. The $E_g$ values for MoO$_3$/SiO$_2$ and MoO$_3$/cAl$_2$O$_3$ are 4.1 eV, consistent with the presence of sub-monolayer dispersed Mo species on these supports [64,65], and in agreement with both the observed PXRD patterns and the Raman spectra. For samples that feature LMCT transitions, all the absorption-edge energies shift to lower values upon incorporation of molybdenum (VI) species. For instance, MoO$_3$/ZrO$_2$ has an $E_g$ value of 3.6 eV, as compared to 5.1 eV for the bare support. This shift is attributed to the presence of oligomeric MoO$_x$ domains on the surface [21,51]. Note that LMCT transitions for support cations and Mo (VI) species do not significantly overlap for MoO$_3$/ZrO$_2$, allowing us to distinguish the edge energies of Mo (VI) and Zr (IV) species. The $E_g$ values

Table 1

| Catalyst (10 wt% nominal loading) | BET surface area of support (m$^2$/g) | BET surface area of catalyst (m$^2$/g) | Oxygen uptake* (μmol/g) | Redox-active Mo species/$b$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$/ZrO$_2$</td>
<td>137.9</td>
<td>117.3</td>
<td>137.9</td>
<td>39.7</td>
</tr>
<tr>
<td>MoO$_3$/TiO$_2$</td>
<td>54.0</td>
<td>54.0</td>
<td>245.0</td>
<td>70.6</td>
</tr>
<tr>
<td>MoO$_3$/CeO$_2$</td>
<td>83.4</td>
<td>29.7</td>
<td>131.0</td>
<td>37.7</td>
</tr>
<tr>
<td>MoO$_3$/cAl$_2$O$_3$</td>
<td>239.2</td>
<td>223.3</td>
<td>43.1</td>
<td>12.4</td>
</tr>
<tr>
<td>MoO$_3$/SiO$_2$</td>
<td>360.0</td>
<td>208.8</td>
<td>98.3</td>
<td>28.3</td>
</tr>
</tbody>
</table>

* $T_{\text{reduction}} = T_{\text{chemisorption}} = 623$ K.

$b$ Calculated as given in Eq. (7).

Fig. 2. Raman spectra of supported MoO$_3$ (10 wt%) catalysts in the Raman shift ranges of (a) 200–1200 cm$^{-1}$ and (b) 750–1050 cm$^{-1}$ normalized by maximum peak intensities for each catalyst in each range. The band at 480 cm$^{-1}$ is due to the glass slide used as a base for holding catalyst samples.

Fig. 3. Hydrogen consumption during temperature programmed reduction (TPR) of supported MoO$_3$ (10 wt%) catalysts. Calcination with O$_2$ at 773 K for 2 h. TPR conditions: 1% H$_2$ flow rate = 50 ml min$^{-1}$, ramp = 2 K min$^{-1}$. Mass of supported catalyst = 400 mg.

Textural properties and oxygen chemisorption values for supported MoO$_3$ catalysts.
also decrease for MoO3/TiO2 and MoO3/CeO2 after incorporation of Mo (VI) species, but not as drastically as for MoO3/ZrO2. The smaller difference in between the support and the weak absorption by the Mo (VI) species, as previously observed for supported V2O5 catalysts [66]. As such, it is difficult to deduce any insights on the local structure of Mo (VI) on these two materials.

3.5. Reactivity studies for comparison of HDO of m-cresol on supported MoO3 catalysts

The product distributions obtained for all the supported catalysts are reported in Table 3 for T = 593 K, a WHSV of 8.27 h⁻¹, and a TOS = 3 h. On an equivalent MoO3 mass basis, conversions for MoO3/ZrO2 and MoO3/TiO2 were 78% and 47%, respectively. In contrast, MoO3/CeO2, MoO3/γ-Al2O3, MoO3/SiO2, and bulk MoO3 yielded conversions of 8%, 13%, 10%, and 13%, respectively. The selectivity to hydrocarbons exceeded 97% for MoO3/ZrO2, MoO3/TiO2, and MoO3/CeO2. On the other hand, MoO3/SiO2 and MoO3/γ-Al2O3 had lower selectivity values to hydrocarbons of 90% and 76%, respectively. Toluene was the only hydrocarbon product generated on all catalysts, except for MoO3/γ-Al2O3, which also generated phenol and dimethyl phenol. Products with ring saturation, such as methyl cyclohexane, were not observed for any catalyst. Taken together, these data indicate that the deoxygenation pathway on all catalysts involved a selective C–O bond cleavage rather than a pathway involving hydrogenation/dehydration as observed for supported noble metals [67], or sequential hydrogenation as observed for MoO3C [68]. The formation of dimethyl phenol on MoO3/γ-Al2O3 may be attributed to transalkylation reactions promoted by acid sites present on the support [30,69]. Control experiments using bare supports showed no appreciable HDO activity for m-cresol, thereby confirming that reactivity arises from the Mo species. Mass balances coupled with gravimetric analyses suggest that less than 1% of the total carbon fed is either transformed to soft coke or incorporated into the MoO3 lattice as carbodic or oxycarbidic species (Table 3), as previously reported for bulk MoO3 [14]. Our data do not allow us to differentiate the carbon in soft coke from the carbon that may be incorporated into the MoO3 domains.

A comparison of initial rates for conversion of m-cresol to toluene is presented in Fig. 4. Rates are normalized in three different ways: (a) per unit mass of MoO3, (b) per total surface area, and (c) per number of oxygen-uptake sites, as described in Eq. (9). MoO3/ZrO2 (~65 mmol h⁻¹ gMoO3⁻¹) and MoO3/TiO2 (~68 mmol h⁻¹ gMoO3⁻¹) featured significantly higher specific rates than all other catalysts tested (Fig. 4(a)). Normalizing rates by surface area shows that MoO3/TiO2 is the most active catalyst (~126 μmol h⁻¹ m⁻²), followed by MoO3/ZrO2 (~55 μmol h⁻¹ m⁻²) and MoO3/γ-Al2O3 (~40 μmol h⁻¹ m⁻²). Both MoO3/SiO2 and MoO3/γ-Al2O3 displayed rates lower than 5 μmol h⁻¹ m⁻². We note that although MoO3/TiO2 has higher initial rates, it features a more abrupt initial deactivation, leading to lower conversions than MoO3/ZrO2 after 1 h on stream, at an equivalent WHSV (see Fig. S7, Supporting Information). STY data show a reactivity trend of MoO3/ZrO2 > MoO3/TiO2 > MoO3/γ-Al2O3 > MoO3/SiO2 > MoO3/CeO2 (see Fig. 4c). After 2 h on stream, the reactivity trend changes to MoO3/ZrO2 > MoO3/γ-Al2O3 > MoO3/TiO2 > MoO3/SiO2 > MoO3/CeO2, due to mainly the fast initial deactivation of MoO3/TiO2 (Fig. S8, Supporting Information).

3.6. Post-reaction catalyst characterization

3.6.1. PXRD and XPS of spent catalysts

PXRD patterns of spent catalysts (TOS = 7.5 h) only show appreciable structural changes for bulk MoO3 and MoO3/TiO2 (Fig. S9, Supporting Information). Indeed, the phase-transformation of bulk MoO3 into a mixture of MoO2 and molybdium oxycarbohydrde (MoOC2H4) has been previously reported by Prasomsri et al. [14]. For MoO3/TiO2, it is observed that the peaks at 2θ = 23.7° and 34.2°, corresponding to crystalline MoO3 nanoparticles, disappear after reaction. However, the formation of bulk molybdium oxycarbohydrde (MoOC2H4) is not detected for the spent MoO3/TiO2 catalysts, indicating that bulk transformations of either unsupported nanoparticles or surface MoO3 domains to MoOC2H4 cannot be detected with PXRD. Note that the peaks corresponding to MoO2 overlap with TiO2 peaks and cannot be resolved.

XPS spectra were acquired on the post-reaction samples (TOS = 7.5 h) to probe the final oxidation states of the surface Mo species (Fig. 5). XPS spectra of pre-reaction samples show the presence of Mo 2p3/2 at 232 eV and Mo 3d5/2 at 229 eV, indicating the presence of MoO3 on all catalysts. After 7.5 h on stream, the XPS spectra show a decrease in the intensity of the Mo (VI) peaks, indicating the formation of MoO2 or MoOx (x < 3) species. The intensity of the Mo (VI) peaks decreases in the order MoO3/ZrO2 > MoO3/TiO2 > MoO3/γ-Al2O3 > MoO3/SiO2 > MoO3/CeO2, as shown in Fig. 5. The decrease in the Mo (VI) peaks is accompanied by the appearance of new peaks at lower binding energies, indicating the presence of MoO2 or MoOx (x < 3) species. The decrease in the Mo (VI) peaks is accompanied by the appearance of new peaks at lower binding energies, indicating the presence of MoO2 or MoOx (x < 3) species. These results are consistent with the decrease in the Mo (VI) peaks observed by XPS, indicating the formation of MoO2 or MoOx (x < 3) species.

Table 2
Absorption-edge energy of supports and supported catalysts (10 wt%) determined from UV–Vis spectroscopy.a,b

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Absorption edge energy of support (eV)</th>
<th>Absorption edge energy of supported catalyst (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO3/ZrO2</td>
<td>5.1</td>
<td>3.6</td>
</tr>
<tr>
<td>MoO3/TiO2</td>
<td>3.6</td>
<td>3.3</td>
</tr>
<tr>
<td>MoO3/CeO2</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>MoO3/γ-Al2O3</td>
<td>n/d</td>
<td>4.1</td>
</tr>
<tr>
<td>MoO3/SiO2</td>
<td>n/d</td>
<td>4.1</td>
</tr>
<tr>
<td>MoO3</td>
<td>n/a</td>
<td>3.1</td>
</tr>
</tbody>
</table>

a Reaction conditions: T = 593 K, Ptotal = 1.013 bar (0.0102 Pfeed balance H2), WHSV = 8.27 h⁻¹, TOS = 3 h.
b Carbon deposition estimated by TPO-MS on spent catalysts at TOS = 7.5 h.

Table 3
Reactivity data for the conversion of m-cresol on bulk and supported MoO3 (10 wt%) catalysts at TOS = 3 h.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (C-mol%)</td>
<td>78</td>
<td>47</td>
<td>8</td>
<td>13</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>Selectivity to hydrocarbons</td>
<td>99</td>
<td>99</td>
<td>97</td>
<td>76</td>
<td>90</td>
<td>99</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Toluene</td>
<td>77</td>
<td>46</td>
<td>7</td>
<td>10</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>Xylene</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxygenates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>22</td>
<td>53</td>
<td>93</td>
<td>87</td>
<td>90</td>
<td>87</td>
</tr>
<tr>
<td>Dimethyl phenol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon deposition*</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1</td>
<td>1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

* Reaction conditions: T = 593 K, Ptotal = 1.013 bar (0.0102 Pfeed balance H2), WHSV = 8.27 h⁻¹, TOS = 3 h.
ence of only Mo$^{6+}$ species. However, the presence of reduced Mo species ($\text{Mo}^{5+}$ and Mo$^{4+}$) is seen across all samples. MoO$_3$/CeO$_2$ shows the highest proportion of Mo$^{6+}$ species (75%), with the remainder present as Mo$^{5+}$ species (25%). The proportion of Mo$^{5+}$ species ranges from 30% to 40% in all other samples. In addition, MoO$_3$/TiO$_2$ features a unique Mo$^{3+}$ species (9%), based on the assignment of binding energies used by Choi and Thompson [70]. Importantly, only ca. 25% of the surface is reduced to Mo$^{4+}$ species for MoO$_3$/ZrO$_2$, MoO$_3$/TiO$_2$, and MoO$_3$/Al$_2$O$_3$, whereas ca. 50% of surface Mo species exist as Mo$^{4+}$ in bulk MoO$_3$ and MoO$_3$/SiO$_2$ after reaction. XPS spectra acquired on another independent set of supported MoO$_3$ samples demonstrate the reproducibility of this trend (Fig. S10, Supporting Information).

3.6.2. Temperature programmed oxidation studies

TPO-MS was performed on the spent catalysts (TOS = 7.5 h) to determine the nature and quantity of carbonaceous species on the catalyst surface (Fig. 6). The CO$_2$ evolution profile for MoO$_3$/ZrO$_2$, MoO$_3$/CeO$_2$, and MoO$_3$/TiO$_2$ occurred in a temperature range between 570 and 750 K, similar to that of bulk MoO$_3$. As such, we posit that the nature of the carbonaceous deposits on these catalyst surfaces is similar and can be attributed to the presence of “soft
catalysts, as reported previously for spent MoO₃ catalysts [14]. MoO₃/γ-Al₂O₃ evolves CO₂ at temperatures greater than 735 K, which can be ascribed to the presence of more refractory graphitic coke. A similar analysis for MoO₃/SiO₂ reveals maximum CO₂ evolution at 640 K, along with a long shoulder that continues beyond 850 K, thus suggesting the presence of both soft coke and graphitic coke. Regeneration of MoO₃/γ-Al₂O₃ and MoO₃/SiO₂ would require calcination temperatures above 750 K, whereas all other supported catalysts would require calcination temperatures below 650 K. The TPO-MS data show that the carbon content of post-reaction MoO₃, MoO₃/SiO₂, MoO₃/γ-Al₂O₃, MoO₃/CeO₂, MoO₃/TiO₂, and MoO₃/ZrO₂ is 5.4, 4.7, 4.9, 0.7, 1.7, and 3.1% of the catalyst weight, respectively. We note that these values may include carbon incorporated into the lattice for any oxycarbide species formed during reaction [14].

3.7. Catalyst stability and regenerability

The catalysts with higher reactivity, MoO₃/ZrO₂ and MoO₃/TiO₂, were selected for long-term stability studies. The supported catalysts were tested over 100 h and were compared with bulk MoO₃ at space velocities that yielded similar conversion values (Fig. 7). The catalysts with higher reactivity, MoO₃/ZrO₂ and MoO₃/TiO₂, were almost identical deactivation rate constants for TOS ranging of 14.5 to 100 h, which translates to a stable period is observed in which conversion only decreased from 65% to 100%, followed by fast deactivation from a conversion of 70% to 34% after 100 h [14]. A first-order deactivation profile can be divided into three zones with deactivation rate constants of 0.305 and 0.039 h⁻¹/C₀ for fresh and 0.006 h⁻¹/C₀ for supported catalysts, respectively. The total site yields (defined as the total moles of toluene formed per mole of redox-active Mo species over the course of the reaction) after 100 h for MoO₃/TiO₂ and MoO₃/ZrO₂ are ca. 440 and 1125, respectively (Fig. S12, Supporting Information). XPS analysis of the spent catalysts shows that the Mo⁶⁺ species in bulk MoO₃ are reduced to Mo⁴⁺ and Mo⁰, with no Mo⁶⁺ peaks left after 70 h on stream (Fig. 8). The C 1s spectra do not show any peaks associated with carbide carbon (Fig. S13, Supporting Information). However, the peaks corresponding to adventitious carbon may subsume the carbidic carbon peak; hence, we cannot completely rule out the formation of Mo₂C. The deactivation of bulk MoO₃ seems to be the result of surface over-reduction to MoO₄⁺ and metallic Mo (Mo⁰). In contrast, Mo species appear to be stabilized in intermediate Mo⁵⁺ and Mo⁶⁺ oxidation states for MoO₃/ZrO₂ and MoO₃/TiO₂. We note that the spent MoO₃/TiO₂ catalyst also contains peaks associated with Mo⁶⁺ species.

Both MoO₃/ZrO₂ and MoO₃/TiO₂ can be regenerated by calcination under O₂ (100 ml min⁻¹) at 673 K for 6 h (Fig. 9). While MoO₃/TiO₂ has almost identical deactivation rate constants pre- and post-regeneration (0.290 and 0.305 h⁻¹ for fresh and regenerated catalysts, respectively), the initial deactivation rate is 2.75 times higher post-regeneration for MoO₃/ZrO₂ (Fig. S14, Supporting Information). Nonetheless, the conversions seem to reach similar steady-state values for the regenerated catalysts. Taken together, the evolution of CO₂ below 673 K during TPO-MS of spent MoO₃/TiO₂ and MoO₃/ZrO₂, and their regenerated activity after calcination at 673 K indicates that the deactivation is reversible, and likely caused by carbonaceous deposits [68,71] and reduction of Mo species to oxidation states with low reactivity (e.g., Mo⁴⁺) [14].

4. Discussion

Reduction of supported molybdenum catalysts has been shown to create coordinatively unsaturated (CU) sites that are active for hydrogenation and hydrodesulfurization (HDS) reactions [72]. In addition, for oxidative desulfurization and vapor-phase ammoniplaysis of 3-picoline to nicotinonitrile, an increase in oxygen chemisorption values was correlated with an increase in activity for supported MoO₃ and V₂O₅ catalysts with CU sites [52,53,60,73]. Past studies for sub-monolayer supported MoO₃ catalysts have considered all surface Mo species to be active when calculating turnover frequencies or STYs for oxidation reactions [25,26,27,59,74]. However, we show that a different number of initial redox-active species calculated from oxygen chemisorption are
observed based on the nature of the support (Table 1). Thus, in contrast to previous studies, the STY values reported here account for the differences in number of redox-active Mo species.

Our previous work on HDO reactions using bulk MoO$_3$ indicated that the reaction could proceed via an oxygen vacancy driven mechanism [13]. We hypothesize that HDO on supported molybdenum catalysts may occur via a similar mechanism, as illustrated in Scheme S1 (Supporting Information). Elucidation of reaction mechanism for conversion of m-cresol to toluene on supported MoO$_3$ catalysts is not the focus of this study. We note that recent studies by Bhan and co-workers on the HDO of anisole and acetone on Mo$_2$C strongly suggest that both metallic and Brønsted acid sites play important roles during reaction upon partial oxidation of the surface [75,76]. The reducibility of Mo species on the support surface should influence the number of oxygen vacancies, and therefore change the reactivity toward HDO. The lower $T_{\text{max}}$ values for MoO$_3$/ZrO$_2$, MoO$_3$/TiO$_2$, and MoO$_3$/Al$_2$O$_3$ suggest higher reducibility (i.e., higher tendency to form CU Mo sites) on these supports. As such, the observed correlation between the lower $T_{\text{max}}$ values with the higher STYs is expected (Fig. 10). The reducibility of dispersed species on support surface has been correlated with reactivity for other redox and vacancy driven reactions, including oxidation of methanol and ethanol, toluene hydrogenation, and oxidative dehydrogenation of propane [23,77–79].

Previous reports have shown that Au and Cu supported on CeO$_2$ have higher acetylene and acetaldehyde oxidation activity than when supported on ZrO$_2$ or TiO$_2$ [80,81]. CeO$_2$ is known to be an “oxygen pump” capable of replenishing oxygen vacancies with
oxygen atoms from the bulk structure [82,83]. Accordingly, our data show that MoO3/CeO2 featured the lowest reactivity for HDO, as Mo species are largely present in their highest oxidation (Mo6+) state (75%) and displayed high T_max values in the H2–TPR. We hypothesize that under the reaction conditions investigated, not enough CU Mo sites are created because they are quickly replenished with oxygen from the CeO2 support. Indeed, migration of oxygen in CeO2 has been shown to take place through a vacancy hopping mechanism [83]. Strong evidence supporting this mechanism is the measured increase in the proportion of Ce3+ state in post-reaction samples (Fig. S15, Supporting Information), suggesting diffusion of oxygen from CeO2 to the surface Mo species.

The prevalence of Mo5+ species in most supported catalysts indicates the presence of CU sites. In bulk MoO3, Mo5+ species arising from either the transformation of MoO3 to Mo6+ or the reduction of MoO3 to Mo3+, have been hypothesized to be responsible for HDO [14]. Although post-reaction PXRD analysis of supported catalysts showed no detectable crystalline oxycarboxyhydrate formation, the presence of Mo5+ species seems to relate to the reactivity. Recently, the presence of Mo5+ species on thermally-reduced single-layer nanostructures of MoO3 grown on Au (1 1 1) was attributed to one-dimensional sheet defects formed by the elimination of bridging oxygen atoms [84]. As opposed to the over-reduction observed in bulk MoO3, the post-reaction XPS clearly shows the stabilization of Mo5+ state for MoO3/ZrO2, as well as Mo6+ and Mo5+ states for MoO3/TiO2 after 100 h on stream. Therefore, the increased stability of MoO3/ZrO2 and MoO3/TiO2 can be attributed to the stabilization of these intermediate Mo species upon dispersion of MoO3 on these supports. Thus, the supports appear to play two key roles: on the one hand, the support allows for CU sites to be formed at lower temperatures (as evidenced by the H2–TPR data), and on the other, it prevents over-reduction to lower oxidation states with lower reactivity.

The differences in STY values across different catalysts suggest support-induced changes in intrinsic activity. With the exception of MoO3/CeO2, the STY values for HDO of m-cresol to toluene increase with decreasing electronegativity of the support cation (Fig. 11). The increasing reactivity with decreasing electronegativity of the support cation has been seen for supported catalysts in redox reactions, such as alcohol oxidation and oxidative dehydrogenation of alkanes [85–89]. For instance, the TOFs for redox reactions, such as alcohol oxidation and oxidative dehydrogenation of ethane followed a reactivity order of MoO3/ZrO2 > MoO3/γ-Al2O3 > MoO3/TiO2 > MoO3/SiO2 which was inversely correlated to the support cation electronegativity [27]. A decreasing cation support electronegativity (SiF4 > AlF3 > TiF4 > ZrF4 > CeF4) increases the electron density of the Mo–O-support bridging oxygen, improving catalytic activity for redox reactions [85,86]. This bond has also been reported to influence reactivity toward acidic products for supported niobium and tantalum oxide catalysts as seen by the inverse trend of increasing reactivity seen with increasing electronegativity of the support cation, due to increasing acidity of the Mo–O-support bridging oxygen [90]. In our case, we hypothesize that the Mo–O-support bridging oxygen atoms play an important role during H abstraction required to initiate the HDO process, similar to other redox reactions [89,91]. Increased reactivity for redox reactions has been ascribed to reduction in activation energy [27], and an increase in the pre-exponential factor on supports with more electropositive cations for oxidative dehydrogenation and alcohol oxidation reactions [85,86,88,89]. Quantum chemical calculations and near-edge X-ray absorption spectroscopy (NEXAFS) studies on oxidative dehydrogenation of methanol to formaldehyde also suggested that the higher reactivity of MoO3 on TiO2 and ZrO2 compared to that on SiO2 and Al2O3 is correlated with the density of accessible electronic states, which ultimately influences the pre-exponential factor of the reaction rate constant [79,92]. The mechanistic origins for the increased reactivity for these redox reactions have been hypothesized to be due to a higher oxygenate steady-state equilibrium adsorption capacity and an easier H abstraction due to increased basicity of Mo–O-support bonds [27,85,86,88,89,92]. We posit that the genesis of the support’s influence on HDO reactivity could be linked to these effects. Considering the electronegativity trend, MoO3/CeO2 should have the highest unoccupied density of states of all catalysts tested, yet it features the lowest activity. As seen from both TPR and post-reaction XPS, the propensity for formation of oxygen vacancies is low on MoO3/CeO2. Computational studies on VOx/CeO2 have indicated the role of CeO2 in stabilizing the highest V5+ state [91]. It is likely that a similar mechanism prevents the reduction of Mo6+ to lower oxidation states, resulting in a decreased number of oxygenate adsorption sites. Overall, our results are consistent with an oxygen vacancy driven mechanism; however, other interpretations cannot be ruled out. Kinetic and in-situ titration studies will be crucial in determining the role of oxygen vacancy, metallic and Bronsted acid sites on bulk and supported MoO3 catalysts for HDO.

The catalyst deactivation on MoO3/ZrO2 and MoO3/TiO2 is shown to be reversible, which is likely caused by coke deposition and reduction of Mo species to oxidation states with lower activity. The refractory coke formation on MoO3/γ-Al2O3 and MoO3/SiO2 is probably catalyzed by surface acidic sites [93]. The trend in the quantity of coke mirrors the trend in the acid strength of supports [94,95]. Indeed, γ-Al2O3 is known to be a strongly acidic support, followed by TiO2, and ZrO2 with weaker acidity [29,96]. The higher quantity and refractory nature of the graphitic coke formed on SiO2 and γ-Al2O3 makes them undesirable for use as supports for HDO.

5. Conclusions

In summary, the effect of metal oxide supports on redox behavior and intrinsic reactivity of Mo species toward HDO of m-cresol to toluene was investigated. All catalysts exhibit high toluene selectivity at a temperature of 593 K and low H2 pressures (<1 bar). Mo species are largely present as oligomeric domains on all supports. The intrinsic HDO activity of Mo species on different supports was compared by normalizing the rate of formation of toluene with the initial moles of redox-active Mo species, as determined by oxygen chemisorption. The catalytic activity toward HDO shows a strong dependence on the reducibility of surface Mo species and the electronegativity of support cation (with the exception of MoO3/CeO2). Our data show that TiO2 and ZrO2 are optimal sup-

![Fig. 11. Initial site time yield (STY) versus support cation electronegativity (Pauling scale) for supported MoO3 (10 wt%) on SiO2, γ-Al2O3, CeO2, TiO2, and ZrO2. Reaction conditions: T = 593 K, P_total = 1.013 bar (0.0102 P_feed, balance H2), WHSV = 8.27 h⁻¹.](Image 1)
ports that promote high activity and improved stability. The supports play an important role in stabilizing specific lower Mo oxidation states. Post-reaction characterization reveals a link between intermediate Mo (Mo\textsuperscript{5+} and Mo\textsuperscript{6+}) states and catalytic activity. The XPS analysis on spent catalysts shows that TiO\textsubscript{2} and ZrO\textsubscript{2} stabilize Mo\textsuperscript{5+} species, in stark contrast to bulk MoO\textsubscript{3}, which reduces to lower oxidation states with lower reactivity. Catalyst deactivation is reversible and likely caused by coke deposition and the reduction of Mo species to oxidation states with lower activity (e.g., Mo\textsuperscript{4+}). Both MoO\textsubscript{2}/ZrO\textsubscript{2} and MoO\textsubscript{2}/TiO\textsubscript{2} can be readily regenerated by calcination with O2 at 673 K. MoO\textsubscript{2}/SiO\textsubscript{2} and MoO\textsubscript{3}/\gamma-Al\textsubscript{2}O\textsubscript{3} exhibit a higher tendency to form refractory graphic coke, thereby requiring higher calcination temperatures for regeneration.

The mechanism of HDO is not conclusive, but reaction rates appear to be related to coordinatively unsaturated Mo sites, as required in an oxygen vacancy driven mechanism. Controlling the reducibility of dispersed active species, along with stabilizing intermediate oxidation states, is critical for developing active and robust oxide-based systems for the HDO of biomass-derived compounds.

**Acknowledgments**

This research was funded by British Petroleum (BP) through the MIT Energy Initiative Advanced Conversion Research Program. The authors would like to thank Justin Nelson, for help with Raman spectroscopy.

**Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.07.034.

**References**

6. T.R. Carlson, G.A. Tompsett, W.C. Conner, G.W. Huber, Aromatic production and CoMo/SiO\textsubscript{2} catalysts using low H\textsubscript{2}.