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# Dynamics of inverse metal oxides on metal catalysts using spectro-kinetics: reversible Brønsted acid site formation and irreversible reduction

Sagar Sourav,<sup>ab</sup> Jiahua Zhou,<sup>bc</sup> Quentin Kim,<sup>bc</sup> Kewei Yu,<sup>id bc</sup>  
Weiqing Zheng<sup>id d</sup> and Dionisios G. Vlachos<sup>id \*cd</sup>

Brønsted acid sites (BASs) in inverse catalysts are vital for the selective hydrogenolysis of polyols, specifically cleaving secondary C–O bonds. These BASs form dynamically *in situ* in an H<sub>2</sub> environment. While H<sub>2</sub> enables rapid BAS generation on short timescales, it reduces the catalyst at prolonged exposures. The active center for BAS generation, the kinetics of BAS formation, its reverse decomposition, and the irreversible oxide reduction have lacked direct experimental evidence. Here, aided by advanced spectro-kinetic studies, we identify trimeric W<sub>3</sub>O<sub>x</sub> sites on Pt as the active centers for BAS generation, whereas isolated WO<sub>x</sub> species on SiO<sub>2</sub> act merely as spectator species, demonstrated using an inverse WO<sub>x</sub>/Pt catalyst as a representative system. A detailed kinetic profile capturing the dynamics of W<sub>3</sub>O<sub>x</sub> sites on Pt is also established. The rate constant for BAS formation is two orders of magnitude higher than for its decomposition, which is one order of magnitude faster than the irreversible site reduction. Co-fed H<sub>2</sub>O suppresses the site reduction by ~50%. Furthermore, the H<sub>2</sub> partial pressure plays an important role. While lower gas-phase H<sub>2</sub> partial pressure does not influence the reversible BAS formation, it can significantly (~3×) suppress catalyst reduction. These findings offer critical insights into optimizing reaction conditions through periodic H<sub>2</sub> pulsing, enhancing catalyst stability and performance in hydrogenolysis reactions.

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## Introduction

Metal–metal oxide (M–MO) catalysts are pivotal in petrochemical, fine chemical, pharmaceutical, and biomass upgrading reactions.<sup>1–8</sup> They typically combine noble metals like Pt, Ir, and Rh with oxophilic metal oxides such as WO<sub>x</sub>, ReO<sub>x</sub>, and MoO<sub>x</sub> on top.<sup>9,10</sup> Their multiple surface functionalities—including Brønsted acid (BAS), Lewis acid (LAS), redox, and metallic sites—enable selective catalysis through synergistic interactions.<sup>3,11,12</sup> Among these, supported WO<sub>x</sub>/Pt inverse catalysts<sup>13,14</sup> have garnered attention for alkane skeletal isomerization,<sup>15</sup> NO<sub>x</sub> reduction,<sup>16</sup> biomass-derived chemical production,<sup>17</sup> and plastic upcycling.<sup>18</sup>

Recent advances employing *in situ/operando* characterization, density functional theory (DFT) calculations,

and probe chemistries have shed light on the structure and functionality of supported WO<sub>x</sub>/Pt catalysts.<sup>9,10,13,14,19</sup> For instance,<sup>19</sup> *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with CO as a probe molecule and high-resolution transmission electron microscopy (HR-TEM) revealed that in oxidizing environments, WO<sub>x</sub> predominantly remains anchored on the SiO<sub>2</sub> support while Pt exists as oxidized PtO<sub>x</sub>. Reduction with CO facilitates the near-complete reduction of PtO<sub>x</sub> without significantly altering the WO<sub>x</sub> anchoring. In contrast, H<sub>2</sub> reduces Pt sites completely and decorates them with WO<sub>x</sub> due to strong metal-support interaction (SMSI). CO-DRIFTS and probe chemistry studies further suggested that well-coordinated Pt sites favor WO<sub>x</sub> decoration, while under-coordinated sites are energetically unfavorable for anchoring WO<sub>x</sub>.<sup>19</sup>

Additional insights from *in situ* Raman spectroscopy and DFT calculations<sup>13</sup> highlighted the conceivable formation of oligomeric, best represented as trimeric W<sub>3</sub>O<sub>x</sub>, species on Pt surfaces, a significant departure from the traditional structure of WO<sub>x</sub> on SiO<sub>2</sub>. On SiO<sub>2</sub> supports, tungsten oxide (WO<sub>x</sub>) exists exclusively as isolated surface species up to the monolayer coverage, beyond which three-dimensional WO<sub>3</sub>

<sup>a</sup> Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India<sup>b</sup> Delaware Energy Institute, University of Delaware, Newark, Delaware 19716, USA<sup>c</sup> Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, USA. E-mail: vlachos@udel.edu<sup>d</sup> Delaware Energy Institute, Center for Plastics Innovation, University of Delaware, Newark, Delaware 19716, USA



### STEM (scanning tunnelling electron microscopy)

STEM imaging was done using a JEOL NEOARM microscope equipped with a spherical aberration corrector and two Energy-Dispersive X-Ray Spectroscopy (EDS) detectors operating at 200 kV. For this, the samples were dispersed using pure acetone solution onto lacey carbon-coated copper grids provided by Electron Microscopy Sciences. The diameter of over 100 particles was measured using the ImageJ software. The surface-weighted mean particle size was then calculated using the formula  $\sum n_i d_i^3 / \sum n_i d_i^2$  ( $d_i$ , particle size;  $n_i$ , number of particles with size  $d_i$ ).

### HR-TEM (high resolution transmission electron microscopy) and HAADF-STEM-EDS (high angle annular dark field- STEM-EDS)

The distribution of Pt and W particles was further probed using a TITAN 80–300 aberration corrected TEM equipped with an EDS detector operating at 300 kV. For this, the samples were dispersed in pure ethanol and added onto lacey carbon-coated copper grids, provided by Electron Microscopy Sciences.

### *In situ* Raman spectroscopy

Raman spectra were collected using a Horiba Jobin Yvon LabRAM high-resolution Raman apparatus equipped with 325, 532, and 633 nm laser excitations and a Sincerity OE detector. The 532 nm wavelength excitation was used to minimize sample damage by laser heating. Sample conditioning was carried out in a home built low void volume *in situ* cell.<sup>29</sup> The cell temperature was precisely controlled by an Omega temperature controller and cooling water flow. The gas flow was adjusted by mass flow controllers (MFCs). Before all experiments, the Raman laser was calibrated using a silicon standard. In a typical experiment, ~15–20 mg of catalyst in powder form was placed inside the sample cup of the *in situ* cell. A total of 150 s, 30 s per scan and 5 scans, were used for spectra acquisition.

*In situ* catalyst pre-treatment was undertaken before the *in situ* Raman measurements, as described below. Sample annealing was done at 673 K for 1 h in pure Ar flow (50 sccm). Sample reduction was undertaken in 10% H<sub>2</sub>/Ar flow (50 sccm) at 673 K for 1 h, followed by purging with pure Ar at 673 K for another 30 minutes. After the pre-treatments, the sample temperature was decreased to 423 K for spectra collection in either pure Ar or 10% H<sub>2</sub>/Ar flow (50 sccm). For catalyst reduction, the sample was additionally exposed to 10% H<sub>2</sub>/Ar (50 sccm) gas flow for 2 h at 423 K.

### CO-DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy)

The CO-DRIFTS experiments were conducted in a Thermo Fisher Nicolet™ iS50 FTIR spectrometer. Sample conditioning was carried out in the Harrick environmental cell HVC-MRA-5. The cell temperature was precisely

controlled by an ATK-024-3 Harrick temperature controller and cooling water flow. The gas flow was adjusted by mass flow controllers (MFCs). In a typical experiment, ~15–20 mg of catalyst in powder form was placed inside the sample cup of the *in situ* cell. 64 scans with a resolution of 4 cm<sup>-1</sup> were used for spectra collection.

The sample pre-treatment was carried out as explained before. After the catalyst reduction and flushing at 673 K, the sample was cooled down to 308 K. 10% CO/Ar (10 sccm) was introduced for 15 minutes, followed by flushing with pure Ar for 30 minutes before spectra collection.

### *In situ* UV-vis spectroscopy

UV-vis spectra were obtained using an Avantes ULS2048CL-EVO UV-vis spectrometer equipped with an AvaLight-XE light source and an adjustable UV/VIS/NIR high-temperature probe. The sample conditioning was carried out in a home built low void volume *in situ* cell. The cell temperature was precisely controlled by an Omega temperature controller and cooling water flow. The sample pre-treatment was done as mentioned for *in situ* Raman spectroscopy studies. For spectra collection after different pre-treatments, a total of 60 s, 0.1 s per scan and averaging over 600 scans, were used for spectral acquisition. BaSO<sub>4</sub> was used as the white reference material whose absorbance was subtracted from the sample absorbance spectra.

### Transient spectroscopy study

Transient spectroscopy studies were conducted with *in situ* UV-vis spectroscopy. In all cases, the samples were pre-reduced and flushed at 673 K as mentioned in the *in situ* Raman spectroscopy experimental procedure. The sample was then cooled to 423 K, where all other investigations were undertaken. For all kinetic measurements, a total of 1 s, 0.1 s per scan and averaging over 10 scans, were used for spectral acquisition. The home built *in situ* cell has a void volume of <1 cc, suggesting the gases have an average residence time of <1.2 s at total flow of 50 sccm.<sup>29</sup>

The modulation excitation UV-visible spectroscopy (ME-UV-vis) experiment was conducted by alternately exposing the catalyst bed to 10% H<sub>2</sub>/Ar for 900 s and pure Ar for 900 s in a cyclic manner (1800 s per cycle). The fast gas switching was ensured by implementing a Vici low dead volume valve with automatic operation functionality. A home-built software was used to analyse the MES data. A total of 5 cycles of gas switching was conducted, out of which the last 3 cycles were averaged for data interpretation. The fundamental frequency ( $f_1$ ) was used to understand the dynamic response of participating sites to feed perturbation.

BAS kinetics were determined by step-jump experiments. In particular, in a 900 s cycle, 10% H<sub>2</sub>/Ar was introduced into the catalyst bed for the first 120 s, and the system was then exposed to pure Ar for the remaining 780 s. An average of 4 cycles were used to process the data. The change in the



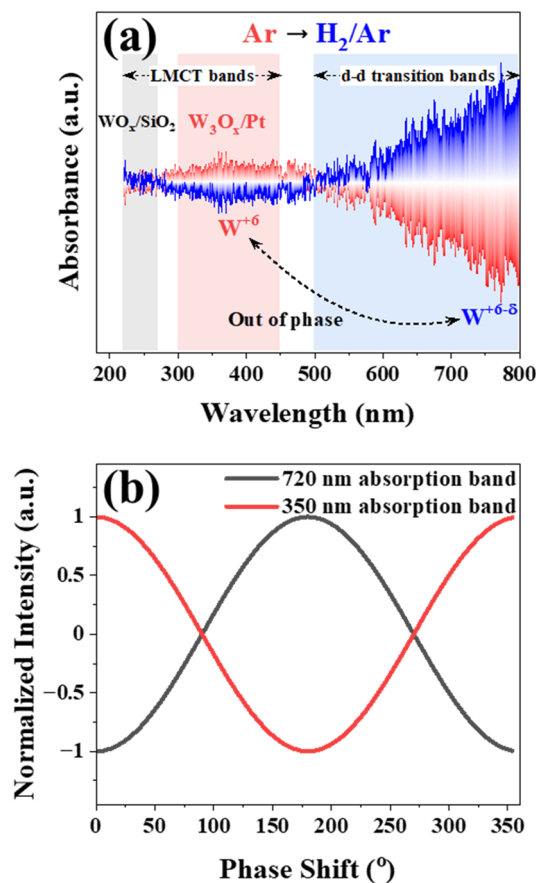


Fig. 1 (a) ME UV-vis phase-resolved spectra of the 4 W-1Pt/SiO<sub>2</sub> catalyst. Cycle length is 1800 s, with the 1st half cycle of 10% H<sub>2</sub>/Ar and 2nd half cycle in pure Ar. Only the fundamental frequency ( $f_1$ ) was used to generate the plot. (b) Phase response of normalized 720 nm and 350 nm band intensities.

absorbance intensity of the 720 nm band (assigned to reduced WO<sub>x</sub> species) was used to measure the kinetics of the processes. A first-order approximation was taken to model the WO<sub>x</sub> hydroxylation to determine the rate constant ( $k_{d(\text{BAS})}$ ) for BAS decomposition as shown in eqn (1). For

determining the rate ( $r_{d(\text{BAS})}$ ) of BAS decomposition, a linear fit of the absorbance was used for the 60 s period (121–180 s) after the gas switching from 10% H<sub>2</sub>/Ar to Ar (refer to Fig. 4 for demonstration.)

$$I(C_{\text{BAS}}) = I(C'_{\text{BAS}}) + I(C_{\text{BAS}_0})\exp(-k_{d(\text{BAS})} \cdot t); \quad (1)$$

where,  $I(C_{\text{BAS}})$  represents the UV-vis intensity of the 720 nm band related to the concentration of BASs at time  $t$ ;  $I(C'_{\text{BAS}})$  is a constant related to the 720 nm band intensity in the absence of any BAS formation;  $I(C_{\text{BAS}_0})$  represents the UV-vis intensity of the 720 nm band related to the concentration of BASs at time 0, initial time;  $k_{d(\text{BAS})}$  is the rate constant for BAS decomposition;  $t$  is time.

To obtain the catalyst reduction kinetics, the sample was exposed to Ar, 10% H<sub>2</sub>/Ar, 2% H<sub>2</sub>/Ar and (10% H<sub>2</sub> + 3% H<sub>2</sub>O)/Ar for different durations. A representative schematic is shown in Fig. S8. After each treatment duration, the rate of BAS decomposition ( $r_{d(\text{BAS})}$ ) was then determined. Since the rate of a chemical reaction is directly proportional to the concentration of the active species, any variation in their concentration is reflected in the overall reaction rate. To quantify this, the relative change in concentration was evaluated by taking the ratio of reaction rates after catalyst conditioning in the above-mentioned gas environments to the rate prior to any conditioning. Specifically, the concentration of available BASs was inferred from the absolute reaction rates measured at defined time intervals. By comparing the rate at time  $t = \Delta t$  to the initial rate at  $t = 0$  (where  $\Delta t$  refers to the duration of catalyst treatment in different gas environments), we estimated the relative decline in the population of BAS-forming sites. This approach enabled us to track the progressive reduction of W<sub>3</sub>O<sub>7</sub>-H species as a function of time and gas environment. Finally, a first-order approximation was employed to model the reduction kinetics of WO<sub>x</sub> species, allowing the determination of the apparent rate constant ( $k_{\text{red}}$ ).



Fig. 2 Time-resolved UV-vis spectra of the 4 W-1Pt/SiO<sub>2</sub> catalyst. The H<sub>2</sub> on-off cycle duration is 900 s, where (a) 10% H<sub>2</sub>/Ar was introduced for the first 120 s and (b) pure Ar for the remaining 780 s.





**Fig. 3** Slow reduction of the 4 W-1Pt/SiO<sub>2</sub> catalyst. (a) BAS decomposition initial rate ratio (of  $\Delta t$  minutes' treatment to no treatment in Ar, 2% H<sub>2</sub>/Ar, 10% H<sub>2</sub>/Ar and (10% H<sub>2</sub> + 3% H<sub>2</sub>O)/Ar) calculated from UV-vis spectroscopy (see Fig. S8 and the associated discussion). (b) Time on stream *t*-butanol activity without H<sub>2</sub> co-feed, and with 2% and 10% H<sub>2</sub> co-feed. The values in the plot represent the percentage decrease in activity after 9 h as compared to the initial activity. (c) *In situ* Raman spectra in 10% H<sub>2</sub>/Ar environment (after 5 and 120 min of treatment). (d) BAS decomposition rate constant ( $k_{d(\text{BAS})}$ ) after 120 minutes' treatment in Ar, 2% H<sub>2</sub>/Ar and 10% H<sub>2</sub>/Ar. All catalysts were pre-reduced at 673 K in 10% H<sub>2</sub>/Ar for 60 min. All experiments were conducted at 423 K.

### CO-pulse chemisorption

The CO pulse chemisorption experiments were carried out in a Micromeritics Autochem-II 2920 analyzer equipped with a TCD detector. In a typical experiment, ~50 mg of powder catalyst was loaded into a quartz U-tube. The catalyst reduction and flushing were conducted at 673 K as described before. The temperature was then decreased to 308 K, and CO adsorption was carried out by pulse injection of 10% CO/He until the sample was saturated. For investigating catalyst reduction, the sample was additionally exposed to 10% H<sub>2</sub>/Ar (50 sccm) gas flow for 2 h at 423 K before cooling down to 308 K.

### *tert*-Butanol dehydration

The *tert*-butanol dehydration was carried out in a fixed bed reactor. 2 mg of the catalyst, diluted by 48 mg of quartz were loaded and put in place by the help of quartz wool.<sup>13</sup> Before the dehydration reaction, the sample was reduced and flushed at 673 K as described before. The temperature was then lowered to 423 K. 4 mol% *tert*-butanol was admitted into the reactor through a customized gas saturator. The total gas flow rate was balanced in N<sub>2</sub> at 100 sccm. *tert*-Butanol

conversion was calculated using eqn (2), as carbon balance of >95% was observed.

$$\begin{aligned} \text{tert-butanol conversion}(\%) \\ = \frac{(\text{tert-butanol in}(\text{mol})) - (\text{tert-butanol out}(\text{mol}))}{(\text{tert-butanol in}(\text{mol}))} \times 100\% \end{aligned} \quad (2)$$

## Results and discussion

We synthesized a library of materials (see Experimental) denoted as  $x\text{W-}y\text{Pt/SiO}_2$ , where  $x$  and  $y$  reflect the weight percent of WO<sub>*x*</sub> and Pt on the SiO<sub>2</sub> support, respectively. Detailed characterization of inverse WO<sub>*x*</sub>/Pt on SiO<sub>2</sub> catalysts is presented in SI section 1 (see Fig. S1–S4 and the associated discussion). In brief, 1Pt/SiO<sub>2</sub> and 0.1Pt/SiO<sub>2</sub> catalysts have Pt particles of comparable sizes, ~1.7–2 nm. Adding WO<sub>*x*</sub> does not significantly alter the Pt particle size, although a slight increase is observed for the 0.1Pt/SiO<sub>2</sub> catalyst. For the 4 W-1Pt/SiO<sub>2</sub> catalyst, reduction at 673 K results in approximately 2/3rd of the exposed Pt surface being decorated by WO<sub>*x*</sub> species, confirming the inverse WO<sub>*x*</sub>/Pt configuration formation. The following uses the 4 W-1Pt/SiO<sub>2</sub> as a representative catalyst.





**Fig. 4** Effect of  $\text{H}_2$  partial pressure on the BAS formation and decomposition on the 4 W-1Pt/SiO<sub>2</sub> catalyst. (a) The BAS decomposition rate  $r_{\text{d}(\text{BAS})}$ , and (b) BAS decomposition rate constant ( $k_{\text{d}(\text{BAS})}$ ) after removal of 10%  $\text{H}_2/\text{Ar}$ . (c) The BAS decomposition rate  $r_{\text{d}(\text{BAS})}$ , and (d) BAS decomposition rate constant ( $k_{\text{d}(\text{BAS})}$ ) after removal of 2%  $\text{H}_2/\text{Ar}$ . The cycle duration is 900 s, where  $\text{H}_2/\text{Ar}$  was introduced for the first 120 s and pure Ar for the remaining 780 s. The  $r_{\text{d}(\text{BAS})}$  was calculated by taking a linear approximation of between 121 and 180 s (60 s duration after  $\text{H}_2$  removal) and  $k_{\text{d}(\text{BAS})}$  was calculated by exponential decay fitting of absorbance data from 121 to 900 s. All catalysts were pre-reduced at 673 K in 10%  $\text{H}_2/\text{Ar}$  for 60 minutes. All experiments were conducted at 423 K.

### Identifying the active site for *in situ* BAS formation

*In situ* Raman and UV-visible spectroscopy reveal that the 4 W-1Pt/SiO<sub>2</sub> catalyst comprises two distinct  $\text{WO}_x$  species: (i) isolated  $\text{WO}_x$  units on the SiO<sub>2</sub> support and (ii)  $\text{W}_3\text{O}_x$  units associated with Pt nanoparticles (see SI section 2, Fig. S5 and the accompanying discussion). These results are consistent with prior reports.<sup>13</sup> To unequivocally identify the active  $\text{WO}_x$  site responsible for forming *in situ* the BASs (see SI section 3 for the detailed discussion), we conducted modulation excitation UV-visible (ME UV-vis) spectroscopy experiments (see Fig. 1). In these experiments, the catalyst bed was alternately exposed to 10%  $\text{H}_2/\text{Ar}$  for 900 s and pure Ar for 900 s in a cyclic manner (1800 s cycle duration). The dynamic response for the  $\text{WO}_x$  structure to feed perturbation was analyzed using the fundamental frequency, providing critical insights into the  $\text{WO}_x$  species under reaction conditions.<sup>30</sup>

Phase-resolved spectra for the 4 W-1Pt/SiO<sub>2</sub> catalyst (Fig. 1a) reveal dynamic changes in the ligand-to-metal charge transfer (LMCT) bands and the  $d-d$  transition region, absent from the 1Pt/SiO<sub>2</sub> and 4 W/SiO<sub>2</sub> catalysts (see SI section 4, Fig. S6 and the associated discussion). Among the

LMCT bands, only those associated with  $\text{W}_3\text{O}_x$  species on Pt (300–450 nm)<sup>13</sup> show variations, whereas the LMCT bands of isolated  $\text{WO}_x$  sites on SiO<sub>2</sub> (220–270 nm)<sup>20,31</sup> remain unchanged during  $\text{H}_2$  switching. This is the first direct experimental evidence of *in situ* BAS formation on selective  $\text{W}_3\text{O}_x$  units on Pt and rules out the participation of isolated  $\text{WO}_x$  sites on SiO<sub>2</sub>.

Interestingly, the LMCT band at ~350 nm and the reduced  $\text{WO}_x$  absorption band at ~720 nm<sup>20</sup> exhibit a 180° phase difference (Fig. 1b). This indicates that the hydroxylation of  $\text{W}_3\text{O}_x$  units on Pt is reversible, where BASs form by gas-phase  $\text{H}_2$  temporarily, and the reduced W centers regain the original oxidation state upon the removal of  $\text{H}_2$  from the gas phase, closing the redox cycle.<sup>13</sup>

### Structural evolution of the 4 W-1Pt/SiO<sub>2</sub> catalyst

The dynamic evolution of the 4 W-1Pt/SiO<sub>2</sub> catalyst is detailed in SI section 2 (see Fig. S5 and the associated discussion). As shown in the previous section,  $\text{W}_3\text{O}_x$  units on Pt exhibit structural dynamics under controlled conditions. Catalyst treatment in  $\text{H}_2$  at 673 K reduces fully oxidized  $\text{W}_3\text{O}_9$  units to



W<sub>3</sub>O<sub>7</sub> units. Subsequently, introducing H<sub>2</sub> at 423 K to the pre-reduced catalyst forms BASs as a W<sub>3</sub>O<sub>7</sub>H configuration.<sup>13</sup>

The correlation between *in situ* Raman and UV-visible experiments indicates that the dynamics of W<sub>3</sub>O<sub>x</sub> sites can be accurately captured using *in situ* UV-visible spectroscopy. In particular, the reversible formation of BASs during periodic H<sub>2</sub> on-off cycling in the catalyst bed can be monitored *via* the intensity of the 720 nm band in the UV-visible spectra (see SI section 2). Given the rapid data acquisition capability of UV-visible spectroscopy (~0.1 s per spectrum) compared to the slower Raman spectroscopy (~several minutes per spectrum), *in situ* UV-visible spectroscopy was employed as the primary tool to investigate the kinetics of reversible BAS formation and decomposition.

#### Kinetics of the formation and decomposition of BASs in the 4 W-1Pt/SiO<sub>2</sub> catalyst

The catalyst was exposed to 10% H<sub>2</sub>/Ar for 120 s, followed by pure Ar for 780 s, in a 900 s cycle. The 720 nm absorption band was monitored to track BAS kinetics, with time-resolved UV-visible spectra presented in Fig. 2, and the intensity evolution of the 720 nm band shown in Fig. S7 (see SI section 5).

Fig. S7 reveals that BASs form within seconds of H<sub>2</sub> introduction, while decomposition upon H<sub>2</sub> removal occurs over 780 s. Assuming first-order kinetics of the BAS decomposition by H atom removal from the -OH group in W<sub>3</sub>O<sub>7</sub>H, the decomposition rate constant ( $k_{d(\text{BAS})}$ ) for the 4 W-1Pt/SiO<sub>2</sub> was estimated as  $5.7 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$  (see Table 1) and for 4 W-0.1Pt/SiO<sub>2</sub>, ( $k_{d(\text{BAS})}$ ) is  $4 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$ . Despite differences in WO<sub>x</sub> distribution (on the SiO<sub>2</sub> support and Pt nanoparticles) between catalysts, the similar  $k_{d(\text{BAS})}$  values confirm that only WO<sub>x</sub> sites on Pt in the inverse WO<sub>x</sub>/Pt configuration undergo dynamic changes, while isolated WO<sub>x</sub> sites on SiO<sub>2</sub> do not. The rapid BAS formation (Fig. S7) suggests that the corresponding rate constant ( $k_{f(\text{BAS})}$ ) is at least two orders of magnitude higher (see Table 1) under the investigated conditions, further highlighting the unique reactivity of WO<sub>x</sub> sites on Pt.

#### Kinetics and origin of slow reduction of the 4 W-1Pt/SiO<sub>2</sub> catalyst

The rate constant for BAS decomposition,  $k_{d(\text{BAS})}$ , reveals information about the nature of the active sites, while the initial decomposition rate is proportional to the concentration of BASs. Variations in the initial BAS

decomposition rates after prolonged exposure to H<sub>2</sub>/Ar *vs.* inert Ar environments shed light on the gradual irreversible reduction of the catalyst at the expense of BASs (see SI section 6). This behavior is captured with the ratio of initial BAS decomposition rates,  $r_{\Delta t}/r_0$ , where  $r_{\Delta t}$  is the rate after treatment duration of  $\Delta t$ , and  $r_0$  is the rate before any treatments (see Fig. 3a).

Exposure to Ar results in no change in  $r_{\Delta t}/r_0$ , whereas treatment with 10% H<sub>2</sub>/Ar rapidly decreases  $r_{\Delta t}/r_0$  within the first 30 min, followed by a slower decline. Assuming a first-order process in the catalyst reduction, driven by the removal of the -OH group from W<sub>3</sub>O<sub>7</sub>H by an H atom to generate W<sub>3</sub>O<sub>6</sub>, we determined the reduction rate constant for site reduction ( $k_{\text{red}}$ , see Table 1). Notably, the  $k_{\text{red}}$  of the 4 W-1Pt/SiO<sub>2</sub> catalyst is an order of magnitude lower than the  $k_{d(\text{BAS})}$  and almost 3 orders of magnitude lower than the  $k_{f(\text{BAS})}$ .

The catalyst reduction is further evident from the decrease in *tert*-butanol dehydration rates; see Fig. 3b. To understand the origin of catalyst reduction, we conducted CO-pulse chemisorption and *in situ* Raman studies. The WO<sub>x</sub> coverage on Pt does not change under prolonged H<sub>2</sub> pre-treatment conditions (see Fig. S3), suggesting the decrease in activity (and BAS concentration) is unrelated to WO<sub>x</sub> migration from the Pt nanoparticles to the SiO<sub>2</sub> support. *In situ* Raman studies reveals that the reduction of WO<sub>x</sub> species occurs specifically on Pt nanoparticles (see Fig. 3c). The terminal W=O (978 and 297 cm<sup>-1</sup> band) is more susceptible to reduction than the bridging W=O. In contrast, W-O-W and Pt-O-W (450 and 837 cm<sup>-1</sup>)<sup>13</sup> remain unaffected. Since BAS formation is associated with terminal W=O bonds,<sup>13</sup> their reduction significantly alters the nature and concentration of BASs. This is supported by the drastic decrease in  $k_{d(\text{BAS})}$  (see Fig. 3d) after H<sub>2</sub>/Ar treatment. This is the first experimental evidence revealing the origin of BAS reduction in WO<sub>x</sub>/Pt inverse catalysts. Furthermore, the above *in situ* Raman characterization demonstrates that the terminal W=O bonds in WO<sub>x</sub>/Pt inverse catalysts are where the BASs form. This finding is further supported by our previous DFT calculations,<sup>14</sup> which showed that H<sub>2</sub> dissociation on terminal W=O bonds is energetically favored by 1.10 eV compared to bridging W-O-W bonds, facilitating BAS formation.

#### Effect of co-feed H<sub>2</sub>O on the reduction kinetics of the 4 W-1Pt/SiO<sub>2</sub> catalyst

Our previous DFT calculations and experimental studies have demonstrated that co-feeding H<sub>2</sub>O enhances BAS density.<sup>14</sup>

**Table 1** Kinetics of formation ( $k_{f(\text{BAS})}$ ), decomposition ( $k_{d(\text{BAS})}$ ) of BASs and slow reduction ( $k_{\text{red}}$ ) of WO<sub>x</sub> species with periodic H<sub>2</sub> on-off and long-term H<sub>2</sub> and H<sub>2</sub> + H<sub>2</sub>O flow, respectively. All catalysts were pre-reduced at 673 K in 10% H<sub>2</sub>/Ar for 60 minutes. The rate constants were determined at 423 K

$k \text{ (s}^{-1}\text{)}$	4 W-1Pt/SiO <sub>2</sub>			4 W-0.1Pt/SiO <sub>2</sub>
	10% H <sub>2</sub> /Ar	2% H <sub>2</sub> /Ar	(10% H <sub>2</sub> + 3% H <sub>2</sub> O)/Ar	10% H <sub>2</sub> /Ar
$k_{f(\text{BAS})}$	$>10^0$			
$k_{d(\text{BAS})}$	$5.7 \pm 0.1 \times 10^{-3}$	$6.5 \pm 0.1 \times 10^{-3}$		$4 \pm 0.1 \times 10^{-3}$
$k_{\text{red}}$	$\sim 7.2 \times 10^{-4}$	$\sim 2.6 \times 10^{-4}$	$\sim 4.9 \times 10^{-4}$	







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