



Title	Effects of oxide platforms on the dynamics and reduction characteristics of hydrogen spillover
Author(s)	Shun, Kazuki; Fujimoto, Akihito; Mori, Kohsuke et al.
Citation	Physical Chemistry Chemical Physics. 2024, 26, p. 28525–28532
Version Type	AM
URL	https://hdl.handle.net/11094/98566
rights	Reproduced from Physical Chemistry Chemical Physics with permission from the Royal Society of Chemistry.
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

ARTICLE

Effects of Oxide Platforms on the Dynamics and Reduction Characteristics of Hydrogen Spillover

Kazuki Shun,^a Akihito Fujimoto,^a Kohsuke Mori,^{*ab} and Hiromi Yamashita^{ab}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The characteristics of hydrogen spillover on various metal oxides, involving the concurrent diffusion of protons (H^+) and electrons (e^-), were systematically studied by combining *in situ* analytical techniques with kinetic analyses. H_2 -temperature programmed reduction and *in situ* X-ray absorption fine structure data showed that hydrogen spillover from Pt onto TiO_2 and WO_3 greatly decreased the temperatures at which Zn^{2+} ions deposited on these remote metal oxides were reduced. In contrast, hydrogen spillover on MgO and CeO_2 did not significantly affect the reduction of remote Zn^{2+} . Mechanisms explaining the effects of spilled hydrogen on reduction for each oxide substrate were proposed based on the dynamic behaviors of H^+ and e^- as ascertained by means of *in situ* spectroscopic characterizations and kinetic analyses. The results of this work indicate that e^- diffusion rather than H^+ diffusion promotes the reduction of deposited metal ions and that interparticle hydrogen spillover can be facilitated over TiO_2 and WO_3 as a consequence of the interfacial diffusion of H^+ and e^- pairs. These findings provide an improved understanding of the hydrogen spillover phenomenon.

Introduction

Hydrogen spillover is a dynamic phenomenon involving the diffusion of coupled protons (H^+) and electrons (e^-).^{1–3} This phenomenon is initiated by the production of atomic hydrogen from gaseous H_2 on noble metal nanoparticles such as Pt, Pd, and Ru followed by their migration onto the support materials⁴. Subsequently, the atomic hydrogen forms the H^+ and e^- pairs and diffuses on the supports driven by increasing configurational surface entropy.⁵ The occurrence of hydrogen spillover has the potential to enhance the performance of materials employed in catalysis,^{6–8} hydrogen storage^{9–11} and fuel cells.^{12–14} One notable feature responsible for these promotional effects is the exceptional reducing power of so-called spilled hydrogen, which enables the simultaneous and uniform reduction of multiple metal ions having distinct reduction potentials.^{15, 16} By taking advantage of this characteristic, advanced multicomponent nanoparticles, such as high-entropy alloys and binary alloys with positive mixing enthalpies, can be synthesized at mild heating rates and at relatively low temperatures.^{17–19}

There have recently been many studies of hydrogen spillover dynamics with the aim of establishing a theoretical basis for this phenomenon.^{20–22} Karim and colleagues reported that spilled atomic hydrogen generated on Pt particles on Al_2O_3 can spill only within a 15 nm radius, whereas migration as far as 1 μm is possible on TiO_2 .²³ Our own group has demonstrated that spilled atomic hydrogen migrates

more readily on TiO_2 and CeO_2 surfaces but moves into the bulk region of WO_3 .²⁴ These different behaviors are attributed to variations in the reducibility of the platform materials.²⁵ On this basis, readily reducible metal oxides such as TiO_2 , CeO_2 and WO_3 are recognized as promising platforms for hydrogen spillover while non-reducible metal oxides, including MgO , Al_2O_3 and SiO_2 , tend to restrict the dynamics of spilled atomic hydrogen.^{26–28} Intriguingly, its effect have been reported to extend outside the oxide particles where noble metal deposited.^{29, 30}

Although various insights into spilled atomic hydrogen dynamics have been accumulated, the reduction characteristics associated with spillover remain poorly understood. However, it has been reported that the reduction of deposited metal ions is significantly promoted on reducible metal oxides,^{23, 27} suggesting that the reduction behavior of spilled atomic hydrogen is also governed by the reducibility of the platform. In fact, the electronic state of spilled atomic hydrogen is determined by the ability of the metal oxide to allow the redox reaction of cations. During spillover, H^+ - e^- pairs are generated on reducible metal oxides according to the reaction $M^{n+} + O^{2-} + H \rightarrow M^{(n-1)+} + OH^-$, whereas only H^+ diffuses on non-reducible metal oxides because these compounds inhibit the diffusion of e^- .^{3, 31} Accordingly, the hydrogen spillover on reducible metal oxides and the H^+ diffusion on non-reducible metal oxide are different in the terms of the electronic state of spilled atomic hydrogen. For these reasons, the reduction behavior associated with spilled hydrogen on a given metal oxide can be investigated by assessing the dynamic behaviors of H^+ and e^- on that compound.

The present work studied the reduction characteristic of spilled hydrogen on various oxides by examining the dynamics of H^+ and e^- , employing physical mixtures of Pt and Zn^{2+} supported on various materials as specimens. The results provide two general insights concerning hydrogen spillover. Firstly, the reduction characteristics

^a Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan. E-mail: K. M. mori@mat.mat.eng.osaka-u.ac.jp

^b Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan.

Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

of spilled atomic hydrogen are evidently affected by e^- diffusion rather than H^+ diffusion. Secondly, the reduction of metal ions can be facilitated by interparticle hydrogen spillover over TiO_2 and WO_3 owing to the readily interfacial diffusion of H^+ and e^- pairs on these oxides. This study provides practical insights and new guidelines for the design of technologies based on hydrogen spillover.

Results & Discussion

Zn^{2+} reduction characteristics on each metal oxide

In order to investigate the effect of hydrogen spillover on the Zn^{2+} reduction characteristics, we contacted Pt^{4+} and Zn^{2+} ions by the physically mixing of Pt/MO_x and Zn/MO_x based on the physical mixture strategy employed in previous work.^{32, 33} TEM results of synthesized $(Pt + Zn)/MO_x$ specimens showed the agglomerated large secondary particles composed of small primary particles, which demonstrates that physically mixed Pt/MO_x and Zn/MO_x are in good contacted with each other, allowing hydrogen spillover from Pt to Zn through their supports (Figure S1). It has previously reported that the occurrence of hydrogen spillover significantly lowers the reduction temperature of deposited metal ions compared with the reduction by the H_2 molecules.^{16, 17, 23} Stated differently, the effects of platform oxides on the reduction characteristic of spilled hydrogen can be evaluated by comparing the reduction temperatures of deposited metal ions in the absence and presence of noble metal nanoparticles initiating hydrogen spillover. Herein, H_2 -TPR data were collected to examine the reduction behavior of Zn^{2+} ions ($E_0(Zn^{2+}/Zn) = -0.763$ V vs. NHE) contained in Zn/MO_x and in physically mixed $(Pt + Zn)/MO_x$ specimens (Figure 1). In the resulting plots, H_2 consumption events contain the reduction of the specimen (i.e. the reduction of deposited ions and the support material) appear as peaks. Each specimen was exposed to the H_2 contained atmosphere prior to H_2 -TPR trials which stabilizes TCD signal. It has been reported that Pt ions reduced below $30^\circ C$,³⁴ and therefore each H_2 consumption in H_2 -TPR profiles exhibits the reduction of either Zn ions or MO_x . The Zn/MgO generated single peaks associated with reduction at 359 and $340^\circ C$ in the absence or presence of Pt, respectively. This result suggests that the reduction behavior of Zn^{2+} did not change even though the Pt was able to promote the dissociation of H_2 molecules. In prior studies, spilled atomic hydrogen diffusing over non-reducible metal oxides such as MgO and Al_2O_3 were found not to significantly affect the reduction of metal cations, consistent with the present work.^{17, 27} In contrast, the reduction temperature shown by the Zn/TiO_2 was decreased by $159^\circ C$ in the presence of Pt, demonstrating the ability of H^+e^- pairs on a reducible metal oxide to

promote the reduction of metal cations, as has been previously reported.^{17, 27} Surprisingly, the reduction temperature for the Zn/CeO_2 was decreased by only $17^\circ C$ following the incorporation of Pt, and so was similar to the value for the non-reducible oxide MgO even though CeO_2 is typically considered a reducible metal oxide. Moreover, the reduction of Zn^{2+} ions and CeO_2 in $(Pt + Zn)/CeO_2$ almost coincided which suggests that the reduction characteristic of hydrogen spillover on CeO_2 is associated with the reduction of CeO_2 . In the case of the Zn/WO_3 , the reduction temperature was decreased by $92^\circ C$ in the presence of Pt, again demonstrating a promotional effect. It should be noted that the reduction temperature of Zn^{2+} on $(Pt + Zn)/MgO$ did not significantly decrease even though the specific surface area of MgO is much smaller than that of TiO_2 where Zn^{2+} ion was promotionally reduced under co-existence of Pt. These results indicate that the reduction characteristic of hydrogen spillover is not affected by the distance between Pt and Zn ions. It is evident from these results that the reduction behaviors of spilled atomic hydrogen species differed between those samples made using non-reducible and reducible metal oxides but also even between the different reducible metal oxides. Because hydrogen spillover involves the concurrent diffusion of H^+ and e^- , the dynamic behaviors of both charged particles on each metal oxide were assessed based on a combination of *in situ* techniques, so as to examine the driving forces for these processes.

Dynamic behavior of spilled atomic hydrogen on MgO

The characteristics of spilled hydrogen on non-reducible metal oxides such as Al_2O_3 and MgO have been widely studied^{26, 35} and some such studies have reported inferior reduction properties compared with reducible metal oxides.^{23, 28} Hence, the research reported herein observed the behavior of spilled hydrogen species on MgO to elucidate the origin of the reduction properties of this material. *In situ* Zn K edge XAFS data were acquired under a D_2 atmosphere at elevated temperatures in trials with both the Zn/MgO and $(Pt + Zn)/MgO$ (Figure 2a). In contrast to the H_2 -TPR analyses, which provided information concerning the reduction behaviors of both the Zn^{2+} ions and platform oxide, the XAFS assessments only monitored the oxidation state of the Zn^{2+} ions. The results indicate that the attenuation of the white line generated by the $(Pt + Zn)/MgO$ was similar to that for the Zn/MgO , suggesting that the presence of Pt did not significantly affect the reduction behavior of the Zn^{2+} , in agreement with the H_2 -TPR findings (Figure 1). The intensity of white line attenuated in accordance with the transition of E_0 position during the reduction treatment (Figure S2). The behavior of spilled

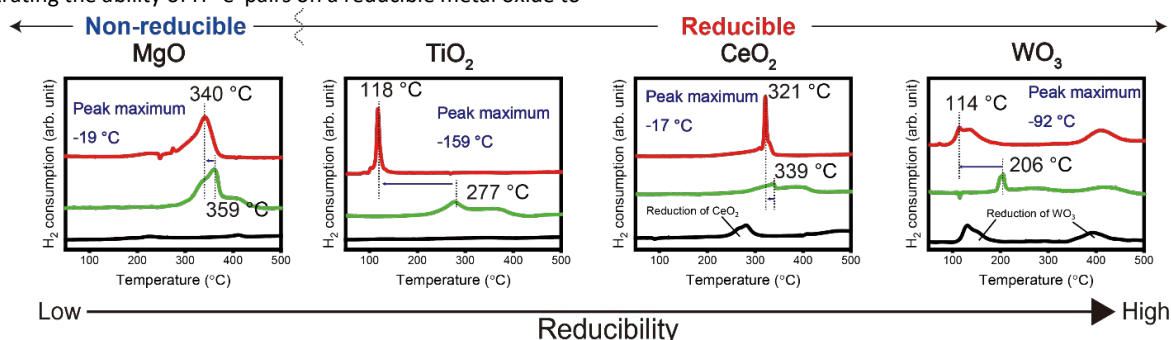


Figure 1. H_2 -TPR profiles for Pt/MO_x (black), Zn/MO_x (green), and $(Pt + Zn)/MO_x$ (red) specimens at a heating rate of $5^\circ C/min$.

atomic hydrogen on the MgO substrate was also examined by acquiring *in situ* DRIFT spectra under D₂ in conjunction with the XAFS experiments (Figure 2b). In the resulting spectra, the diffusion of D⁺ ions can be monitored by observing the peaks related to O²⁻-D⁺ stretching vibrations ($\delta_{\text{O-D}}$) in the range of 2800-2600 cm⁻¹.^{36, 37} It should be noted that this peak evolved during D₂ dosage and attenuated during H₂ dosage which demonstrates that the $\delta_{\text{O-D}}$ was evolved by the proton diffusion phenomenon (Figure S3). The dominant $\delta_{\text{O-D}}$ peak was observed at 150 °C, confirming that proton diffusion readily took place over the MgO at temperatures above 150 °C. This temperature range is lower by 80 °C compared with that for the onset of the reduction of the deposited Zn²⁺, as demonstrated by the E₀ transition in the Zn K edge XANES spectra shown in Figure 2c. It should be noted that the electronic state of reduced Zn is not related to the effect of hydrogen spillover, but is affected by the acid-base property of the support materials,³⁸ therefore we herein assessed at what temperature the E₀ of XANES start to shift. In this way, the E₀ transitions for the Zn/MgO and (Pt + Zn)/MgO were observed within almost the same temperature ranges (Figure S4). That is, spilled atomic hydrogen on MgO did not significantly promote the reduction of deposited Zn²⁺ ions. It has previously been reported that dissociated atomic hydrogen diffuses as H⁺ over non-reducible metal oxides because the cations of these oxides are too irreducible to accept e⁻, meaning that e⁻ diffusion is inhibited.²⁶ Thus, the inhibited reduction of deposited Zn²⁺ on MgO as observed in this work is attributed to the fact that H⁺ ions were not accompanied by e⁻ due to the low reducibility of cations in the MgO. The dynamic behaviors of H⁺ and e⁻ on reducible metal oxides whose cations are relatively easy to reduce were subsequently investigated to obtain additional insights.

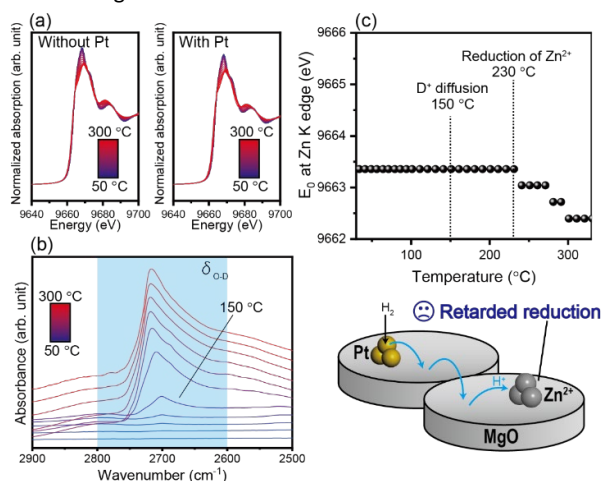


Figure 2. (a) Zn K edge *in situ* XANES spectra of Zn/MgO (left) and (Pt + Zn)/MgO (right) obtained under D₂ at various temperatures. (b) *In situ* DRIFT spectra of (Pt + Zn)/MgO acquired under D₂ at various temperatures. (c) The E₀ transition in the XANES data within the Zn K edge region for (Pt + Zn)/MgO during D₂ reduction (top) and the proposed dynamic behavior of atomic hydrogen species spilled on MgO (bottom).

Dynamic behavior of hydrogen spillover on TiO₂

Hydrogen spillover on TiO₂ is known to have a strong reducing effect and so this effect is widely utilized in a variety of functional catalysts.^{32, 39, 40} Even so, there are insufficient experimental data

concerning the origin of this reduction behavior. The present work therefore examined the manner in which hydrogen spillover on TiO₂ affected the reduction of Zn²⁺ ions. In the case of the *in situ* Zn K edge XANES spectra acquired under D₂ at elevated temperatures, the white line intensity generated by the (Pt + Zn)/TiO₂ was rapidly attenuated at approximately 50 °C whereas the intensity for the pure Zn/TiO₂ gradually decreased as the temperature was increased (Figure 3a). Additionally, the E₀ transitions for the (Pt + Zn)/TiO₂ were observed at lower temperature range than Zn/TiO₂ (Figure S5). These results demonstrated that hydrogen spillover on the TiO₂ contributed to the reduction of the Zn²⁺ ions, which was consistent with the H₂-TPR data (Figure 1a). The dynamic behaviors of D⁺ and e⁻ were investigated by obtaining *in situ* DRIFT spectra under D₂ (Figure 3b). Above 80 °C, a $\delta_{\text{O-D}}$ peak associated with D⁺ diffusion was observed in the (Pt + Zn)/TiO₂ spectra. It can be assumed that the broadening of the $\delta_{\text{O-D}}$ peak represents the inhomogeneity of the O²⁻-D⁺ dipole state derived from oxygens in various coordination states. On the other hand, an intense peak appeared at 1300 cm⁻¹ in the spectra acquired at temperatures as low as 30 °C. It was previously reported that an e⁻ generated by hydrogen spillover was transferred to the midgap states (MGSs) below conduction band (CB) of TiO₂ and excited from MGSs to CB by an irradiation of infrared light.^{41, 42} We have previously observed a broad IR absorption band in a range of 2000–1000 cm⁻¹ for Pt/TiO₂ under H₂ reduction condition, corresponding to e⁻ diffusion via MGS driven by hydrogen spillover.⁴³ Considering the decrease in absorbance in the range of 1600–1400 cm⁻¹, which was attributed to the desorption of H₂O and HOD at elevated temperatures,³⁶ the peak observed in the present work can be assigned to the trapping of e⁻ in MGSs located below the TiO₂ conduction band. Presumably, e⁻ were able to diffuse over the TiO₂ at temperatures as low as 30 °C even though the $\delta_{\text{O-D}}$ peak was only observed above 80 °C, suggesting that e⁻ diffusion was preceded by H⁺ diffusion. Moreover, as shown in Figure 3c, the E₀ transition in the Zn K edge XANES spectra resulted not from H⁺ diffusion but rather from e⁻ diffusion. Consequently, it is likely that the diffusion of e⁻ (rather than that of H⁺) over the TiO₂ enhanced the reduction of Zn²⁺, which also explains the retarded reduction of Zn²⁺ on MgO. Based on the results for MgO and TiO₂, it can be estimated that the dynamic behavior of e⁻ has a greater effect on the reduction behavior of spilled atomic hydrogen than that of H⁺.

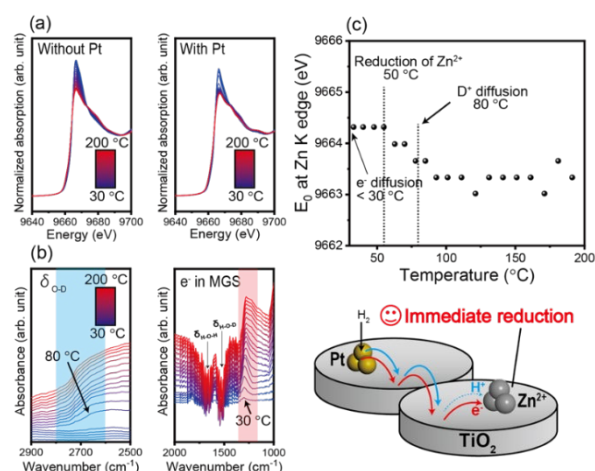


Figure 3. (a) Zn K edge *in situ* XANES spectra obtained from Zn/TiO₂ (left) and (Pt + Zn)/TiO₂ (right) under D₂ at various temperatures. (b) *In situ* DRIFT

spectra obtained from (Pt + Zn)/TiO₂ under D₂ at various temperatures, showing the regions associated with O-D bonding (left) and e⁻ in MGSs (right). (c) The E₀ transition of the XANES data within the Zn K edge region for (Pt + Zn)/TiO₂ under D₂ (top) and the proposed dynamic behavior of atomic hydrogen species spilled on TiO₂ (bottom).

Dynamic behavior of hydrogen spillover on CeO₂

CeO₂ is a promising platform material for catalysts due to the exceptional redox properties and shape-controllable nature of this material.⁴⁴ The hydrogen spillover characteristics of this oxide have also been examined in recent years because this phenomenon can greatly improve the performance of various catalysts.^{45, 46} The present work assessed the reduction performance of CeO₂ in terms of the dynamics of H⁺ and e⁻ diffusion and the associated effects on the reduction of deposited ions. *In situ* DRIFT data were obtained to monitor the dynamics of H⁺ and e⁻ on (Pt + Zn)/CeO₂ (Figure 4a). The appearance of a δ_{O-D} peak attributable to D⁺ diffusion on the CeO₂ substrate was observed above 150 °C, as has been previously reported.²⁴ Notably, this peak sharpened above 300 °C, indicating an increase in the intensity of O²⁻-D⁺ stretching vibrations and the homogenization of the O²⁻-D⁺ dipole states owing to the surface relaxation of CeO₂ surface.⁴⁵ A peak related to the evolution of Ce³⁺ was also observed around 2100 cm⁻¹ at temperatures above 250 °C.^{47, 48} The formation of Ce³⁺ is associated with a continuous e⁻ donation from hydrogen to Ce⁴⁺. These results demonstrate that hydrogen spillover involving the concomitant diffusion of H⁺ and e⁻ pairs took place on (Pt + Zn)/CeO₂ at about 250 °C, even though Zn²⁺ ions on (Pt + Zn)/CeO₂ did not undergo reduction below 300 °C (Figure 1). To obtain information concerning the thermodynamics of hydrogen spillover on CeO₂, the activation energies for the reduction of Zn²⁺ (E_a) on the (Pt + Zn)/MO_x specimens (MO_x = TiO₂, CeO₂ or WO₃) were evaluated using the Kissinger equation based on H₂-TPR data generated at various heating rates (Figure 4b and Figures S6 and S7).⁴⁹ Interestingly, the E_a for CeO₂ was calculated to be 96.5 kJ/mol and so was more than 70 kJ/mol greater than the values for TiO₂ and WO₃. It can be assumed that the rate-determining step for the reduction of Zn²⁺ by hydrogen spillover from Pt deposited on the remote platform was specific for CeO₂. Another possibility is that spilled H⁺-e⁻ pairs on the CeO₂ were less reductive than those on other reducible metal oxides. To clarify this, additional H₂-TPR data were acquired for a specimen in which Pt⁴⁺ and Zn²⁺ were both loaded on CeO₂ (Figure S8). Interestingly, a peak attributable to the reduction of Zn²⁺ appeared between 150 and 250 °C even though Zn²⁺ deposited on (Pt + Zn)/CeO₂ was only reduced above 300 °C. This result demonstrates that intraparticle hydrogen spillover took place on the CeO₂ above 150 °C and that the spilled H⁺-e⁻ pairs on this substrate were able to reduce Zn²⁺ at a lower temperature compared with the temperature required for reduction by gaseous H₂. It is therefore evident that intraparticle hydrogen spillover on the CeO₂ was the rate-determining step for the reduction of Zn²⁺ deposited on this material. This explains the sharp δ_{O-D} peak in Figure 4a, which resulted from interparticle hydrogen spillover from Pt/CeO₂ to Zn/CeO₂. This spillover increased the total number of O²⁻-D⁺ bonds on the (Pt + Zn)/CeO₂. Lee and coworkers previously demonstrated that the formation of Ce³⁺ in response to H₂ exposure was facilitated in a mixture of CeO₂ loaded with Pt and pure CeO₂ following

reduction under H₂ at 400 °C. This effect occurred because boundaries formed between CeO₂ particles provided pathways for interparticle hydrogen spillover due to sintering in the initial reducing H₂ atmosphere.⁴⁵ This insight also suggests that interparticle hydrogen spillover, the driving force for the reduction of Zn²⁺ ions remote from Pt on the substrate, will only occur at high temperature on pristine CeO₂ because of a lack of such boundaries at low temperatures. The reduction characteristics and dynamics of spilled hydrogen on CeO₂ are depicted diagrammatically in Figure 4c. Intraparticle hydrogen spillover involving the diffusion of H⁺ and e⁻ was observed on CeO₂ loaded with Pt above 250 °C. However, the reduction of Zn²⁺ deposited on remote CeO₂ was negligible up to 250 °C where intraparticle hydrogen spillover occurred because interparticle hydrogen spillover was prohibited. At approximately 300 °C, boundaries evolved between CeO₂ particles that provided hydrogen spillover pathways from Pt to Zn²⁺ due to the sintering of the oxide.

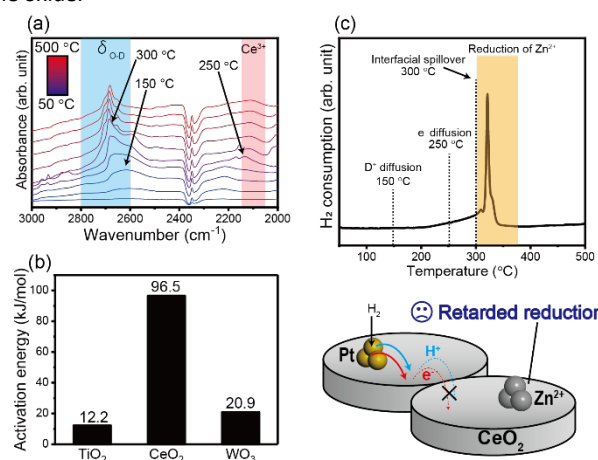


Figure 4. (a) *In situ* DRIFT spectra acquired from (Pt + Zn)/CeO₂ under D₂ at various temperatures showing the O-D (blue) and Ce³⁺ (right) regions. (b) Activation energies for the reduction of Zn²⁺ in each (Pt + Zn)/MO_x specimen as calculated based on Kissinger plots. (c) The H₂-TPR profile obtained for (Pt + Zn)/CeO₂ labeled to indicate hydrogen spillover and the reduction of Zn²⁺ (top) and the proposed dynamic behavior of atomic hydrogen species spilled on CeO₂ (bottom).

Dynamic behavior of hydrogen spillover on WO₃

Hydrogen spillover on WO₃ has been known for over 50 years and has been employed to produce photo- and electrocatalysts.^{1, 50, 51} This phenomenon can facilitate the reduction of deposited metal ions²⁴ although the origin of the driving force for this process remains unclear. Herein, the reduction behavior of hydrogen spillover is disentangled from the dynamics of H⁺ and e⁻ diffusion. *In situ* XAFS measurements for Zn/WO₃ and (Pt + Zn)/WO₃ demonstrated the promoted reduction of Zn²⁺ under the co-existence of Pt (Figure S9), which is consistent to the tendency of H₂-TPR. Therefore, the hydrogen spillover, the simultaneous diffusion of H⁺ and e⁻, on WO₃ can behave as a strong reduction agent. The H⁺ diffusion characteristics on WO₃ were investigated by monitoring the evolution of the δ_{O-D} peak in *in situ* DRIFT spectra acquired under D₂ (Figure 5a). An intense δ_{O-D} peak appeared at 100 °C that was related to H⁺ diffusion on the surface of the WO₃. We previously reported

that H^+ preferentially diffuses into the bulk region rather than the surface in the case of WO_3 .²⁴ Therefore, H^+ ions likely diffused into the WO_3 below 100 °C. Note that the decay of this δ_{O-D} peak may have been due to the formation of D_2O as a consequence of the condensation of O-D groups on the surface.⁵² The extent of e^- diffusion over the (Pt + Zn)/ WO_3 surface was also studied by acquiring *in situ* UV-visible spectra under H_2 , as shown in Figure 5b. The WO_3 was found to change color from yellow to bronze upon accepting e^- based on mixing of the W^{6+} and W^{5+} valence transfer bands. Thus, the visible light absorption of this specimen could be utilized to study hydrogen spillover, meaning coupled H^+ and e^- diffusion.^{53, 54} The WO_3 exhibited visible light absorption based on the formation of W^{5+} above 50 °C, providing evidence for e^- diffusion. Considering that H^+ diffusion occurred below 100 °C, hydrogen spillover involving simultaneous H^+ and e^- diffusion appears to have taken place on this oxide beginning at approximately 50 °C. The absorption of visible light was found to decrease beginning at 75 °C with no increases from 100 to 175 °C, confirming the competitive supply and consumption of e^- on the WO_3 . The temperature region where visible light absorption by WO_3 did not increase in the *in situ* UV-vis spectra corresponds to that where the reduction peak was observed in the H_2 -TPR data (Figure 5c). From these results, it can be assumed that the diffusion of H^+ - e^- pairs over the WO_3 was responsible for the reduction of Zn^{2+} . Hydrogen spillover on WO_3 was evidently slower than that on TiO_2 because there was no increase in the visible light absorbance of WO_3 during the reduction of Zn^{2+} , presumably because the greater reducibility of W^{6+} resulted in the capture of e^- .

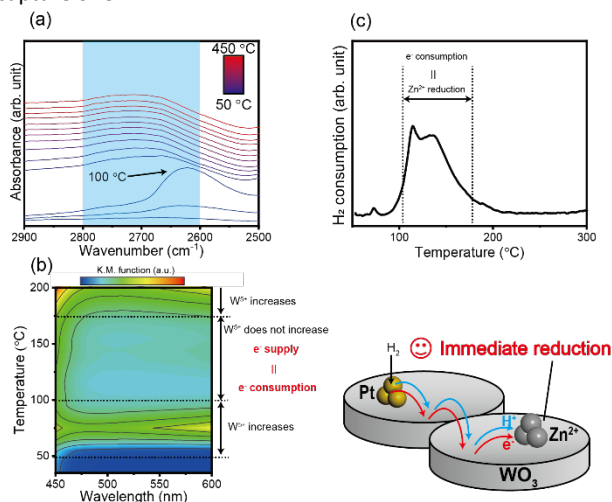


Figure 5. (a) *In situ* DRIFT spectra acquired from (Pt + Zn)/ WO_3 under D_2 at various temperatures in the O-D region. (b) Visible light absorption data showing the presence of W^{5+} within a Pt/ WO_3 specimen as obtained by an *in situ* UV-visible method during reduction under H_2 . (c) The H_2 -TPR profile obtained for (Pt + Zn)/ WO_3 labeled to indicate hydrogen spillover and the reduction of Zn^{2+} (top) and the proposed dynamic behavior of atomic hydrogen species spilled on WO_3 (bottom).

Discussion

Based on the present *in situ* observations of the movements of H^+ and e^- , varying dynamic behaviors were found to take place during hydrogen spillover with differences even between reducible metal

oxides, which have been considered promising platform materials. This section examines the manner in which these oxides affect the dynamics and reduction behavior of spilled atomic hydrogen and addresses the factors that allow hydrogen spillover to promote reduction (Figure 6). In the case of TiO_2 and WO_3 , Zn^{2+} was reduced at approximately 100 °C under H_2 in the case that remote Pt was present to initiate hydrogen spillover. This promotional effect was derived from interparticle e^- diffusion accompanied by H^+ migration from Pt particles to remote Zn^{2+} ions. That is, hydrogen spillover on typical reducible metal oxides permits e^- diffusion as a consequence of the readily reducibility of the cations in such materials. In contrast, Zn^{2+} was reduced only above 300 °C under H_2 after Pt loading on MgO and CeO_2 . In trials using MgO, Zn^{2+} was not reduced even though H^+ diffusion took place. It has been reported that e^- diffusion on non-reducible metal oxides is hindered because of the low reducibility of the associated cations.²⁶ Thus, the minimal reducing power of spilled hydrogen species on MgO can be attributed to a lack of e^- diffusion accompanying the H^+ diffusion. The reduction of Zn^{2+} by hydrogen spillover on CeO_2 did not occur at low temperatures even though both H^+ and e^- were found to diffuse on this material. This outcome was ascribed to the large activation energy for interparticle hydrogen spillover on CeO_2 (Figure 4b). Therefore, the retarded reduction of Zn^{2+} separated from Pt on CeO_2 is evidently a consequence of the inhibited interparticle hydrogen spillover.

The above results suggest two general insights concerning hydrogen spillover. Firstly, the reduction characteristics of spilled atomic hydrogen greatly depend on the dynamics of e^- diffusion rather than H^+ diffusion. Therefore, the reducibility of the platform material is a crucial factor to consider when hydrogen spillover is utilized for the reduction of metal ions. Secondly, there is possibility that hydrogen spillover is inhibited between interfaces even in the case of reducible metal oxides. Accordingly, it should be noted that interparticle hydrogen spillover is not always equivalent to intraparticle hydrogen spillover.

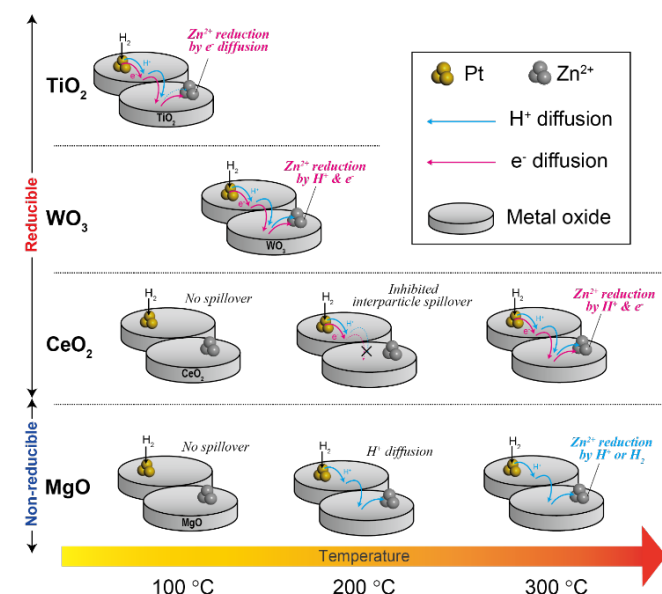


Figure 6. Proposed dynamic behaviors of spilled H^+ and e^- on each metal oxide platform at various temperatures and the associated effects on the reduction of Zn^{2+} .

Conclusions

The present work studied the hydrogen spillover phenomenon on typical metal oxides based on assessing the dynamics and reduction characteristics of H^+ and e^- . Based on systematic characterizations and analyses, a general and important insight on hydrogen spillover, the reduction characteristics of spilled atomic hydrogen are greatly affected by the e^- diffusion dynamics rather than by the H^+ diffusion properties of platform materials, was obtained. In this way, the e^- diffusion favorably occurs in conjunction with the H^+ diffusion on TiO_2 and WO_3 which significantly promotes the reduction of remote metal ions. On the other hand, the e^- diffusion coupled with H^+ is inhibited on MgO and CeO_2 due to its low reducibility or the difficulty in the interparticle diffusion which results in the retarded reduction of distant metal ions, respectively. These findings provide not only crucial insight on the dynamic behavior of spilled H^+ and e^- on various platform materials but also opportunity which promotes understanding of their reduction characteristics.

Experimental

Materials

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ($\geq 98.5\%$ pure) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$ pure) were purchased from Nacalai Tesque. JRC-TIO-6 [rutile TiO_2 , Brunauer–Emmett–Teller (BET) surface area (S_{BET}) = $92.2 \text{ m}^2 \cdot \text{g}^{-1}$] and JRC-CEO-2 (CeO_2 , S_{BET} = 135.3) were both kindly supplied by the Catalyst Society of Japan. WO_3 (99.5% pure, S_{BET} = 5.5) and MgO ($\geq 99\%$ pure, S_{BET} = 2.5) were obtained from Wako Pure Chemical Industries, Ltd. All commercially-available chemicals were used as received.

Synthetic procedures

Pt/MO_x specimens used in this work (where $\text{MO}_x = \text{MgO}$, TiO_2 , CeO_2 or WO_3) were synthesized using a conventional impregnation method. Briefly, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.0335 g) was added to a mixture of MO_x (1.0 g) and distilled water (100 mL) with stirring. The resulting suspension was further stirred at room temperature for more than 1 h after which the water was evaporated by heating the material at 60°C under vacuum to yield Pt/MO_x (containing $1.25 \text{ wt}\%$ Pt^{4+}). The Zn/MO_x specimens (containing $5 \text{ wt}\%$ Zn^{2+}) were obtained using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the precursor via the same procedure employed to produce the Pt/MO_x . The Pt/MO_x and Zn/MO_x were grinded with an agate mortar at a 1:1 mass ratio for 3 min into a homogeneous powder prior to each trial to obtain the $(\text{Pt} + \text{Zn})/\text{MO}_x$.

Characterization

TEM images were obtained with a field emission (FE) instrument (HF-2000, Hitachi). H_2 -temperature programmed reduction (TPR) analyses were conducted using a BEL-CAT instrument (MicrotracBEL Corp.). During these trials, 20 mg specimens were heated from 50 to 500°C at rates of 2, 5 or $10^\circ/\text{min}$ under a 5.0% H_2/Ar flow. Prior to each H_2 -TPR trial, a 5.0% H_2/Ar gas was dosaged to sample holder at 50°C to stabilize TCD signal. Zn K-edge *in situ* X-ray absorption fine structure (XAFS) data were obtained in the transmission mode at the 01B1 beamline station within the SPring-8 facility operated by JASRI in Harima, Japan (proposal no. 2023A1933), employing a Si (111)

monochromator. In a typical experiment, spectra were recorded while a pelletized sample was held in a batch-type *in situ* XAFS cell and heated at $5^\circ\text{C}/\text{min}$ from 50 to 400°C under a 5.0% D_2/He flow. The resulting data were processed using the ATHENA program (Demeter). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained with a Bruker Vertex 70 instrument (Bruker Corp.) equipped with a CaF_2 window during the *in situ* XAFS analyses. *In situ* UV-visible spectra were acquired with a V-750 spectrometer (JASCO International Co., Ltd.) while heating specimens at a rate of $5^\circ\text{C}/\text{min}$ from 50 to 400°C under a H_2 flow.

Author Contributions

K.S. performed the characterization and wrote the manuscript. A.F. performed the catalyst preparation and helped the characterization. K.M. supervised the project. H.Y. helped supervise the project. The manuscript was written through the discussion with all authors. All authors have given approval to the final version of manuscript.

Data availability

The data that support the findings of this study are available from the corresponding author (K.M.) upon reasonable request.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The present work was supported by Grants-in-Aid for Scientific Research (A24H003950 and T22K189200) from the Japan Society for the Promotion of Science (JSPS). K.S. thanks JSPS for a Research Fellowship for Young Scientists (no. 23KJ1506). The synchrotron radiation experiments providing XAFS and DRIFT data were performed at the BL01B1 beamline within the SPring-8 facility with the approval of JASRI (proposal no. 2023A1933).

Notes and references

1. S. Khoobiar, *J. Phys. Chem.*, 1964, **68**, 411-412.
2. M. Li, W. Yin, J. Pan, Y. Zhu, N. Sun, X. Zhang, Y. Wan, Z. Luo, L. Yi and L. Wang, *Chem. Eng. J.*, 2023, **471**, 144691.
3. R. Prins, *Chem. Rev.*, 2012, **112**, 2714-2738.
4. K. Shun, K. Mori, T. Kidawara, S. Ichikawa and H. Yamashita, *Nat. Commun.*, 2024, **15**, 6403.
5. A. Mahdavi-Shakib, T. N. Whittaker, T. Y. Yun, K. B. Sravan Kumar, L. C. Rich, S. Wang, R. M. Rioux, L. C. Grabow and B. D. Chandler, *Nat. Catal.*, 2023, **6**, 710-719.
6. R. Maeda, H. Sampei, R. Nakayama, T. Higo, Y. Koshizuka, Y. Bando, T. Komanoya, Y. Nakahara and Y. Sekine, *RSC Adv.*, 2024, **14**, 9869-9877.
7. C. Mao, J. Wang, Y. Zou, G. Qi, J. Y. Yang Loh, T. Zhang, M. Xia, J. Xu, F. Deng, M. Ghossoub, N. P. Kherani, L. Wang, H. Shang, M. Li, J. Li, X. Liu, Z. Ai, G. A. Ozin, J. Zhao and L. Zhang, *J. Am. Chem. Soc.*, 2020, **142**, 17403-17412.
8. Q. Zhu, H. Zhou, L. Wang, L. Wang, C. Wang, H. Wang, W.

- Fang, M. He, Q. Wu and F.-S. Xiao, *Nat. Catal.*, 2022, **5**, 1030-1037.
9. R. T. Yang and Y. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 4224-4226.
10. N. Kostoglou, C.-W. Liao, C.-Y. Wang, J. N. Kondo, C. Tampaxis, T. Steriotis, K. Giannakopoulos, A. G. Kontos, S. Hinder, M. Baker, E. Bousser, A. Matthews, C. Rebholz and C. Mitterer, *Carbon*, 2021, **171**, 294-305.
11. Y. Li and R. T. Yang, *J. Am. Chem. Soc.*, 2006, **128**, 8136-8137.
12. S.-H. You, S.-M. Jung, K.-S. Kim, J. Lee, J. Park, H. Y. Jang, S. Shin, H. Lee, S. Back, J. Lee and Y.-T. Kim, *ACS Energy Lett.*, 2023, **8**, 2201-2213.
13. Q. He, L. Zeng, L. Han, M. M. Martin, J. Peng, J.-F. Li, A. Oleinick, I. Svir, C. Amatore, Z.-Q. Tian and D. Zhan, *J. Am. Chem. Soc.*, 2021, **143**, 18419-18425.
14. J. Zhang, X. Liu, Y. Ji, X. Liu, D. Su, Z. Zhuang, Y.-C. Chang, C.-W. Pao, Q. Shao, Z. Hu and X. Huang, *Nat. Commun.*, 2023, **14**, 1761.
15. N. M. Briggs, L. Barrett, E. C. Wegener, L. V. Herrera, L. A. Gomez, J. T. Miller and S. P. Crossley, *Nat. Commun.*, 2018, **9**, 3827.
16. K. Shun, S. Matsukawa, K. Mori and H. Yamashita, *Small*, 2024, **20**, 2306765.
17. K. Mori, N. Hashimoto, N. Kamiuchi, H. Yoshida, H. Kobayashi and H. Yamashita, *Nat. Commun.*, 2021, **12**, 3884.
18. N. Hashimoto, K. Mori and H. Yamashita, *J. Phys. Chem. C*, 2023, **127**, 20786-20793.
19. K. Mori, K. Miyawaki and H. Yamashita, *ACS Catal.*, 2016, **6**, 3128-3135.
20. Y. Liu, R. Zhang, L. Lin, Y. Wang, C. Liu, R. Mu and Q. Fu, *Nat. Commun.*, 2023, **14**, 613.
21. M. D. Marcinkowski, A. D. Jewell, M. Stamatakis, M. B. Boucher, E. A. Lewis, C. J. Murphy, G. Kyriakou and E. C. H. Sykes, *Nat. Mater.*, 2013, **12**, 523-528.
22. T. Kamada, T. Ueda, S. Fukuura, T. Yumura, S. Hosokawa, T. Tanaka, D. Kan and Y. Shimakawa, *J. Am. Chem. Soc.*, 2023, **145**, 1631-1637.
23. W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinici and J. A. van Bokhoven, *Nature*, 2017, **541**, 68-71.
24. K. Shun, K. Mori, S. Masuda, N. Hashimoto, Y. Hinuma, H. Kobayashi and H. Yamashita, *Chem. Sci.*, 2022, **13**, 8137-8147.
25. A. Beck, P. Rzepka, K. P. Marshall, D. Stoian, M. G. Willinger and J. A. van Bokhoven, *J. Phys. Chem. C*, 2022, **126**, 17589-17597.
26. R. Prins, V. K. Palfi and M. Reiher, *J. Phys. Chem. C*, 2012, **116**, 14274-14283.
27. S. Masuda, K. Shun, K. Mori, Y. Kuwahara and H. Yamashita, *Chem. Sci.*, 2020, **11**, 4194-4203.
28. S. S. E. Collins, M. Cittadini, C. Pecharromán, A. Martucci and P. Mulvaney, *ACS Nano*, 2015, **9**, 7846-7856.
29. K. Motokura, *Chem. Asian J.*, 2024, e202301083.
30. C. Dong, R. Mu, R. Li, J. Wang, T. Song, Z. Qu, Q. Fu and X. Bao, *J. Am. Chem. Soc.*, 2023, **145**, 17056-17065.
31. T. Matsuda, R. Ishibashi, Y. Koshizuka, H. Tsuneki and Y. Sekine, *Chem. Commun.*, 2022, **58**, 10789-10792.
32. H. Kim, J. H. Park, J.-M. Ha and D. H. Kim, *ACS Catal.*, 2023, **13**, 11857-11870.
33. S. K. Beaumont, S. Alayoglu, C. Specht, N. Kruse and G. A. Somorjai, *Nano Lett.*, 2014, **14**, 4792-4796.
34. S. H. Park, M. S. Tzou and W. M. H. Sachtler, *Applied Catalysis*, 1986, **24**, 85-98.
35. S. Lee, H. Kim, R. Ryoo, J. Y. Park and M. Choi, *Nano Res.*, 2022, **15**, 10357-10365.
36. T. Whittaker, K. B. S. Kumar, C. Peterson, M. N. Pollock, L. C. Grabow and B. D. Chandler, *J. Am. Chem. Soc.*, 2018, **140**, 16469-16487.
37. S. Wang, Z.-J. Zhao, X. Chang, J. Zhao, H. Tian, C. Yang, M. Li, Q. Fu, R. Mu and J. Gong, *Angew. Chem. Int. Ed.*, 2019, **58**, 7668-7672.
38. Y. V. Larichev, B. L. Moroz and V. I. Bukhtiyarov, *Appl. Surf. Sci.*, 2011, **258**, 1541-1550.
39. H. Kang, L. Zhu, S. Li, S. Yu, Y. Niu, B. Zhang, W. Chu, X. Liu, S. Perathoner, G. Centi and Y. Liu, *Nat. Catal.*, 2023, **6**, 1062-1072.
40. Y. Yamazaki, T. Toyonaga, N. Doshita, K. Mori, Y. Kuwahara, S. Yamazaki and H. Yamashita, *ACS Appl. Mater. Interfaces*, 2022, **14**, 2291-2300.
41. D. A. Panayotov and J. T. Yates, *J. Phys. Chem. C*, 2007, **111**, 2959-2964.
42. D. A. Panayotov, S. P. Burrows, J. T. Yates, Jr. and J. R. Morris, *J. Phys. Chem. C*, 2011, **115**, 22400-22408.
43. Y. Yamazaki, K. Mori, Y. Kuwahara, H. Kobayashi and H. Yamashita, *ACS Appl. Mater. Interfaces*, 2021, **13**, 48669-48678.
44. N. Hashimoto, K. Mori, S. Matsuzaki, K. Iwama, R. Kitaura, N. Kamiuchi, H. Yoshida and H. Yamashita, *JACS Au*, 2023, **3**, 2131-2143.
45. J. Lee, P. Tieu, J. Finzel, W. Zang, X. Yan, G. Graham, X. Pan and P. Christopher, *JACS Au*, 2023, **3**, 2299-2313.
46. A. Beck, D. Kazazis, Y. Ekinici, X. Li, E. A. Müller Gubler, A. Kleibert, M.-G. Willinger, L. Artiglia and J. A. van Bokhoven, *ACS Nano*, 2023, **17**, 1091-1099.
47. C. Binet, M. Daturi and J.-C. Lavalley, *Catal. Today*, 1999, **50**, 207-225.
48. C. Binet, A. Badri and J.-C. Lavalley, *J. Phys. Chem.*, 1994, **98**, 6392-6398.
49. H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702-1706.
50. Y. F. Li, N. Soheilnia, M. Greiner, U. Ulmer, T. Wood, F. M. Ali, Y. Dong, A. P. Yin Wong, J. Jia and G. A. Ozin, *ACS Appl. Mater. Interfaces*, 2019, **11**, 5610-5615.
51. J. Chen, C. Chen, M. Qin, B. Li, B. Lin, Q. Mao, H. Yang, B. Liu and Y. Wang, *Nat. Commun.*, 2022, **13**, 5382.
52. J. M. Kim, S. M. Chang, S. M. Kong, K.-S. Kim, J. Kim and W.-S. Kim, *Ceram. Int.*, 2009, **35**, 1015-1019.
53. H. Cheng, M. Wen, X. Ma, Y. Kuwahara, K. Mori, Y. Dai, B. Huang and H. Yamashita, *J. Am. Chem. Soc.*, 2016, **138**, 9316-9324.
54. C. Wang, E. Guan, L. Wang, X. Chu, Z. Wu, J. Zhang, Z. Yang, Y. Jiang, L. Zhang, X. Meng, B. C. Gates and F.-S. Xiao, *J. Am. Chem. Soc.*, 2019, **141**, 8482-8488.

TOC Graphics

The interparticle hydrogen spillover can be facilitated over TiO_2 and WO_3 as a consequence of the interfacial diffusion of H^+ and e^- pairs, while the e^- diffusion coupled with H^+ is inhibited on MgO and CeO_2 .

