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## New monoclinic ruthenium dioxide with highly selective hydrogenation activity†

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Catalytic hydrogenation of aromatic compounds is an important industrial process, particularly for the production of many petrochemical and pharmaceutical derivatives. This reaction is mainly catalyzed by noble metals, but rarely by metal oxides. Here, we report the development of monoclinic hydrogen-bearing ruthenium dioxide with a nominal composition of  $H_xRuO_2$  that can serve as a standalone catalyst for various hydrogenation reactions. The hydrogen-bearing oxide was synthesized through the water gas shift reaction of CO and  $H_2O$  in the presence of rutile  $RuO_2$ . The structure of  $H_xRuO_2$  was determined by synchrotron X-ray diffraction and density functional theory (DFT) studies. Solid-state  $^1H$  NMR and Raman studies suggest that this compound possesses two types of isolated interstitial protons.  $H_xRuO_2$  is very active in hydrogenation of various arenes, including liquid organic hydrogen carriers, which are completely converted to the corresponding fully hydrogenated products under relatively mild conditions. In addition, high selectivities (>99%) were observed for the catalytic hydrogenation of functionalized nitroarenes to corresponding anilines. DFT simulations yield a small barrier for concerted proton transfer. The facile proton dynamics may be key in enabling selective hydrogenation reactions at relatively low temperature. Our findings inspire the search for hydrogen-containing metal oxides that could be employed as high-performance materials for catalysts, electrocatalysts, and fuel cells.

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## Introduction

Heterogeneous catalytic hydrogenation is an important industrial process in which hydrogenation is carried out with molecular hydrogen ( $H_2$ ) in the presence of a catalyst. Typical catalysts are based on noble metal nanoparticles (NPs) such as platinum (Pt),<sup>1</sup> palladium (Pd),<sup>2</sup> rhodium (Rh),<sup>3</sup> and ruthenium (Ru),<sup>4</sup> which are immobilized on a support with a large surface area. The supported NPs are active in a wide range of hydrogenation reactions under relatively mild conditions, but do not always ensure high selectivity for the

desired product. This reduced selectivity is mainly due to the high reactivity of noble metal NPs. To tune the reactivity of active metal NPs, individual atoms dispersed in reducible oxides have been investigated and found to be selective hydrogenation catalysts in many important reactions.<sup>5,6</sup> Notably, it has been found that the active site of the hydrogenation reaction is not a pure metal, but an oxidized metal species. Somorjai and colleagues reported that oxygen strongly bound to the platinum surface affects the selectivity as well as the activity of a hydrogenation reaction.<sup>7</sup> Catalytically active sites may thus be neither metals nor metal oxides, but may be in between.

Metal oxides generally act as supports or promoters for the active catalyst. In fact, metal oxides used as sole catalysts are rare, especially in hydrogenation reactions. Surprisingly, cerium oxide ( $CeO_2$ ) turned out to be an efficient catalyst for gaseous hydrogenation from alkyne to olefin without the need for noble metals.<sup>8</sup> Spectroscopic studies on well-ordered  $CeO_2$  films in combination with density functional theory (DFT) calculations suggest that oxygen vacancies within  $CeO_2$  play a crucial role in the incorporation of hydrogen (H) into the bulk and promote hydrogenation reactions.<sup>9</sup> Numerous efforts have been made to investigate the interaction between hydrogen and metal oxides,<sup>10–12</sup> but little is known about the

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potential of hydrogen insertion to confer metal oxides with superior catalytic activity under ambient conditions. Thus, it is desirable to investigate H-bearing metal oxides as candidates for selective hydrogenation catalysts.

Here, we present the synthesis, characterization, and catalytic activity of a new H-bearing ruthenium dioxide denoted as  $H_xRuO_2$ . Ru-based catalysts have been continuously studied because of the lower cost of Ru compared to Pd and Pt as well as the superior catalytic activity for a wide range of reactions. Moreover, they have been regarded as one of the most active catalysts for several industrially important reactions. The inclusion of hydrogen in reducible ruthenium oxide is exceptional and unprecedented. Unlike rutile  $RuO_2$ ,  $H_xRuO_2$  acts as a standalone catalyst and exhibits excellent activity in the hydrogenation of various arenes and nitro-arenes. Moreover, the  $H_xRuO_2$  catalyst is recyclable and maintains structural integrity in both alkaline and acidic media. This combination of superior activity and high stability can be beneficial for the use of  $H_xRuO_2$  in a wide range of potential applications, especially in catalysis and energy-related fields.

## Results and discussion

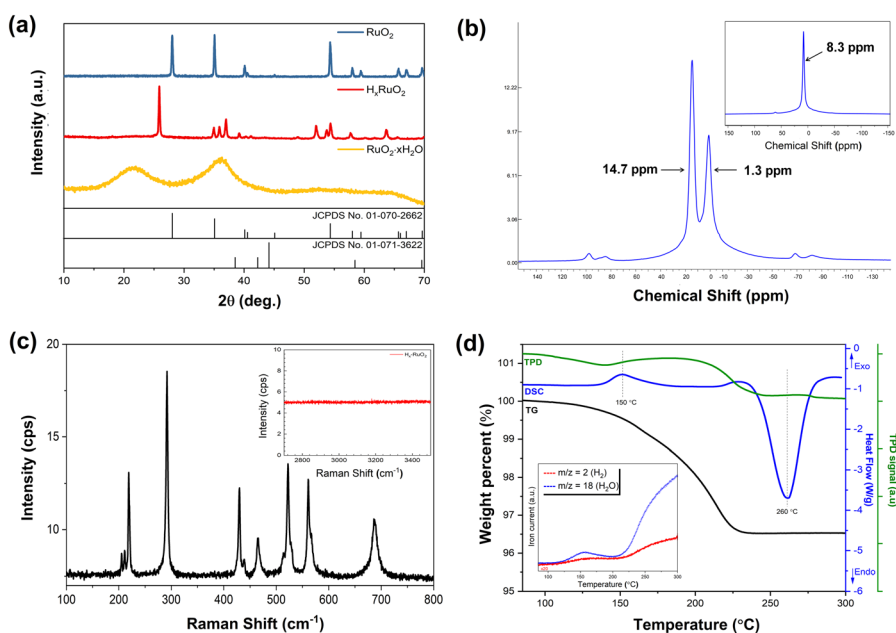
### Synthesis and characterization of $H_xRuO_2$

Hydrogen insertion requires special reaction conditions because annealing metal oxides under a hydrogen atmosphere typically forms metals or oxygen-deficient oxides

rather than H-inserted oxides. Several specialized methods are known for the synthesis of H-inserted oxides, including high-pressure high-temperature techniques,<sup>13</sup> hydrogen spillover,<sup>14</sup> electrochemical hydrogenation,<sup>15</sup> and acid treatment.<sup>16</sup> However, these methods did not succeed in inserting hydrogen into ruthenium dioxide ( $RuO_2$ ). We have developed a soft chemical approach based on the water gas shift reaction, which produces gaseous hydrogen at the expense of carbon monoxide ( $CO + H_2O \rightleftharpoons CO_2 + H_2$ ).<sup>17</sup> The reaction was performed at temperatures below 200 °C to prevent the formation of Ru NPs and to gently insert hydrogen into the host oxide lattice.

Fig. 1a shows powder X-ray diffraction (XRD) patterns of newly synthesized  $H_xRuO_2$ , rutile  $RuO_2$ , and hydrous  $RuO_2 \cdot xH_2O$ . The XRD spectrum of  $H_xRuO_2$  shows several distinct peaks that do not match those of known materials, indicating that  $H_xRuO_2$  adopts a new phase. A structural change might occur upon the insertion of hydrogen into the rutile  $RuO_2$  matrix. The successful synthesis of  $H_xRuO_2$  demonstrates the occurrence of hydrogen spillover on oxide surfaces, followed by chemical and structural transformations induced by coupled proton-electron transfer.<sup>18</sup> Although the formation mechanism is currently not well understood, the insertion reaction appears to be facilitated by oxygen vacancies in ruthenium dioxide.<sup>19</sup>

The presence of hydrogen in  $H_xRuO_2$  was confirmed by solid-state  $^1H$  NMR spectroscopy, which is a powerful technique capable of determining hydrogen species and their



**Fig. 1** Phase identification, spectroscopic characterization, and thermal analysis of  $H_xRuO_2$ . (a) Powder XRD profiles of newly synthesized  $H_xRuO_2$ , rutile  $RuO_2$ , and hydrous  $RuO_2 \cdot xH_2O$ . Vertical lines on the bottom panel show the positions and intensities for  $RuO_2$  and Ru taken from the JCPDS powder diffraction file. (b) Solid-state  $^1H$  MAS NMR spectrum for  $H_xRuO_2$  showing two distinct peaks at 1.3 and 14.7 ppm. The inset is the  $^1H$  MAS NMR spectrum for  $RuO_2 \cdot xH_2O$ . (c) Raman spectra of  $H_xRuO_2$ . The inset shows an expanded view of the Raman spectrum for  $H_xRuO_2$  at higher frequencies. (d) Combined TGA (black line), DSC (blue line), TPD-MS (green line) curves for typical  $H_xRuO_2$  sample as a function of temperature. The large mass change corresponds to the conversion of  $H_xRuO_2$  to  $RuO_2$ , which is accompanied by an endothermic signal in DSC and a water release in TPD-MS. The inset is MS signals of  $H_2O$  (blue line) and  $H_2$  (red line) obtained from the TPD-MS measurement.



chemical environment in the oxide framework. Fig. 1b shows the magic angle spinning (MAS)  $^1\text{H}$  NMR spectrum for  $\text{H}_x\text{-RuO}_2$ , illustrating two peaks at 1.3 and 14.7 ppm. For comparison, we measured the  $^1\text{H}$  NMR spectrum for hydrous  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  (see inset). The single broad peak at 8.3 ppm is attributed to water, suggesting that the two peaks in  $\text{H}_x\text{-RuO}_2$  are not ascribed to protons in the structural water moiety. Based on the analysis of  $^1\text{H}$  NMR involved in hydrogen bonding,<sup>20</sup> one peak at 14.7 ppm can be assigned to protons involved in the hydrogen bond, while the other signal at 1.3 ppm can be attributed to interstitial protons interacting weakly with neighboring oxygen and ruthenium atoms. The experimentally obtained chemical shifts are in good agreement with those computed *via* DFT for structure models with interstitial protons, as discussed in the ESI.†

Raman spectroscopy was used to obtain additional information about the crystal structure and chemical bonding of  $\text{H}_x\text{-RuO}_2$ , whose Raman spectrum (Fig. 1c) displays a new set of sharp peaks below  $800\text{ cm}^{-1}$ , but no signals in the range of  $800$  to  $4000\text{ cm}^{-1}$ . This indicates that neither signals attributed to the hydroxyl (O–H) group nor the water H–O–H moiety are observable in  $\text{H}_x\text{-RuO}_2$ .<sup>21</sup> Below  $800\text{ cm}^{-1}$  the calculated spectrum of the most stable structure identified *via* DFT calculations, a  $P2_1/c$  symmetry  $\text{RuO}_2\text{H}$  phase, was in good agreement with experiment (Fig. S1†). However, at higher wavenumbers it possessed peaks associated with O–H wagging and stretching modes, not seen in experiment. As described below, first principles molecular dynamics (FPMD) calculations suggest that O–H $\cdots$ O to O $\cdots$ H–O proton exchange ought to be facile in this structure at room temperature. This can result in broadening of the O–H peaks, making them experimentally undetectable.

The chemical environments of Ru and O were evaluated by X-ray photoelectron spectroscopy (XPS). Particularly, the oxidation state of Ru and the bonding nature of O were examined through XPS analysis. The XPS spectra of  $\text{H}_x\text{-RuO}_2$  are shown in Fig. S2† and were analyzed based on the published literature for common Ru materials.<sup>22</sup> The fitting of the O 1s peak clearly indicates the presence of hydrogen that interacts with oxygen. The broad 3d peak structure, which can be fitted with several symmetric curves, suggests the presence of multiple oxidation states including  $\text{Ru}^{3+}$  and  $\text{Ru}^{4+}$  ions. The Ru metal peak, which usually appears around  $280.0\text{ eV}$ , was not detected.

### Thermal analysis

To obtain quantitative information on the hydrogen stoichiometry in  $\text{H}_x\text{-RuO}_2$ , thermogravimetric analysis (TGA) was conducted. Differential scanning calorimetry (DSC) and temperature programmed desorption-mass spectrometry (TPD-MS) measurements were also performed to evaluate the thermal stability of  $\text{H}_x\text{-RuO}_2$ . Fig. 1d shows typical TGA, DSC, and TPD-MS curves for  $\text{H}_x\text{-RuO}_2$ , collected in an inert gas atmosphere, as a function of temperature. The TGA curve shows a gradual weight loss up to about  $230\text{ }^\circ\text{C}$  and no

further weight loss above  $230\text{ }^\circ\text{C}$ . The DSC curve exhibits a weak exothermic peak at  $150\text{ }^\circ\text{C}$  and a distinct endothermic peak related to water loss at  $260\text{ }^\circ\text{C}$ . The exothermic peak appears to be associated with the structural transition from monoclinic to orthorhombic or tetragonal due presumably to hydrogen loss. The endothermic DSC signal at  $260\text{ }^\circ\text{C}$  corresponds well with a significant weight loss observed in the TGA curve. Moreover, the temperature-dependent tendency of the TPD curve is very similar to those of the TGA and DSC curves.

As shown in the inset of Fig. 1d,  $\text{H}_2\text{O}$  ( $m/z = 18$ ) evolution was clearly observed in the TPD-MS curve, which follows weight changes on the TGA curve. In addition to  $\text{H}_2\text{O}$  signals,  $\text{H}_2$  ( $m/z = 2$ ) gas evolution was detected. The  $\text{H}_2\text{O}$  mass spectrum shows a small peak at around  $150\text{ }^\circ\text{C}$  and a large peak starting at around  $230\text{ }^\circ\text{C}$ , which also agrees with the TGA and DSC curves.

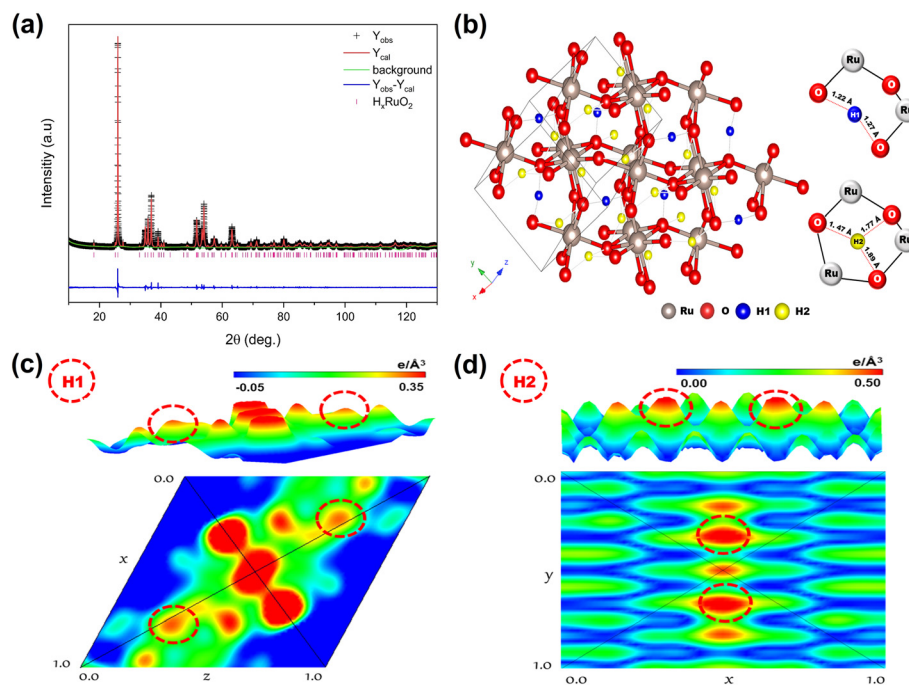
To determine the exact content of hydrogen in  $\text{H}_x\text{-RuO}_2$ , TGA measurements were performed in air using five different samples prepared under identical conditions (Fig. S3†). The average weight loss calculated from the TGA data was  $6.61\%$ . The overall composition can be established as  $\text{H}_x\text{-RuO}_2$  ( $x = 0.98$ ), which corresponds to nearly one equivalent of hydrogen per formula unit.

### Structural characterization

The structure of  $\text{H}_x\text{-RuO}_2$  was determined from Rietveld refinement of high-resolution synchrotron XRD data using the computationally predicted monoclinic  $P2_1/c$   $\text{RuO}_2\text{H}$  structure described in the ESI† as a starting model. First, we refined the positions of the Ru and O atoms and then two partially occupied H positions were included in the refined structure. A Fourier map constructed from the difference between the observed pattern and hydrogen-free refined structural model was employed to determine the positions of the hydrogen atoms.<sup>23,24</sup> Two non-equivalent positions, H1 and H2, were found and their parameters were refined until a satisfactory fit was obtained. The occupation factors of the H1 and H2 sites were set to 0.49 each, based on the TGA data. This  $P2_1/c$  model, including hydrogen positions, fit superbly to the synchrotron XRD data. Fig. 2a shows the Rietveld refinement of the synchrotron data to the model, which includes the observed, calculated, and difference diffraction patterns. The final refined structure is illustrated in Fig. 2b. As seen in Fig. 2c and d, the locations of the hydrogen atoms are imaged as dotted red circles that have high residual electron densities. The final crystallographic data and structural parameters are shown in Table S1†. Selected interatomic distances and angles are given in Table S2†.

Unlike the rutile structure with four long ( $2.026\text{ \AA}$ ) and two short ( $1.869\text{ \AA}$ ) Ru–O bonds,<sup>25</sup>  $\text{H}_x\text{-RuO}_2$  has a distorted monoclinic structure with six different Ru–O bonds ranging from  $1.993$  to  $2.148\text{ \AA}$ . Two short and long Ru $\cdots$ Ru distances,  $2.519$  and  $3.149\text{ \AA}$ , alternate along the  $c$  axis. A notable feature is the shortest Ru $\cdots$ Ru separation ( $2.519\text{ \AA}$ ), which is





**Fig. 2** Structural characterization of  $H_xRuO_2$ . (a) Rietveld refinement profile of  $H_xRuO_2$ . Observed (black crosses) and calculated (red solid line) synchrotron XRD intensities for  $H_xRuO_2$ . Vertical bars show the Bragg peak positions. The difference plot is shown at the bottom. (b) The schematic structures for  $H_xRuO_2$ . The structure is drawn so that the location of the H atoms can be easily seen. Gray and red spheres denote ruthenium and oxygen atoms, respectively. The Ru atoms occupy distorted  $RuO_6$  octahedral sites. Hydrogen (H) atoms are represented by small spheres, where H1 and H2 are blue and yellow spheres, respectively. (c) The difference Fourier map of  $H_xRuO_2$  in cross section with H1, showing the change in hydrogen distribution in H1. The dotted circles in maps (c and d) indicate the positions of H atoms. (d) The difference Fourier map of  $H_xRuO_2$  in cross section with H2, showing the change in hydrogen distribution in H2.

comparable to the Ru–Ru bond length (2.650 Å) in hexagonal Ru metal, indicating the presence of metallic Ru–Ru bonds. The H1 proton interacts closely with two oxygen atoms at distances of 1.224 and 1.269 Å, while the H2 proton interacts weakly with three oxygen atoms at distances of 1.474 to 1.889 Å (Fig. 2b). These bonding properties are consistent with the aforementioned spectroscopic results.

### Hydrogenation of arenes catalysed by $H_xRuO_2$

To test the catalytic activity of  $H_xRuO_2$ , we began our investigation by evaluating the hydrogenation of toluene. Toluene was chosen as the model substrate because it is considered an efficient liquid organic hydrogen carrier (LOHC).<sup>26</sup> Catalytic hydrogenation was performed without solvent in an autoclave. For comparison, toluene

hydrogenation activity was also tested using rutile  $RuO_2$  and commercial Ru catalyst. The commercial catalyst, 5 wt% of Ru loaded onto  $Al_2O_3$  ( $Ru@Al_2O_3$ ), is widely used as a catalyst for numerous hydrogenation reactions. The surface areas of rutile  $RuO_2$ ,  $H_xRuO_2$ , and  $Ru@Al_2O_3$  determined from the Brunauer–Emmett–Teller (BET) analysis, are 4.0, 27.8 and 118.9  $m^2 g^{-1}$ , respectively (Fig. S4†). Typical SEM images of  $H_xRuO_2$  (Fig. S5†) indicate micron-sized powders, which are consistent with the BET data.

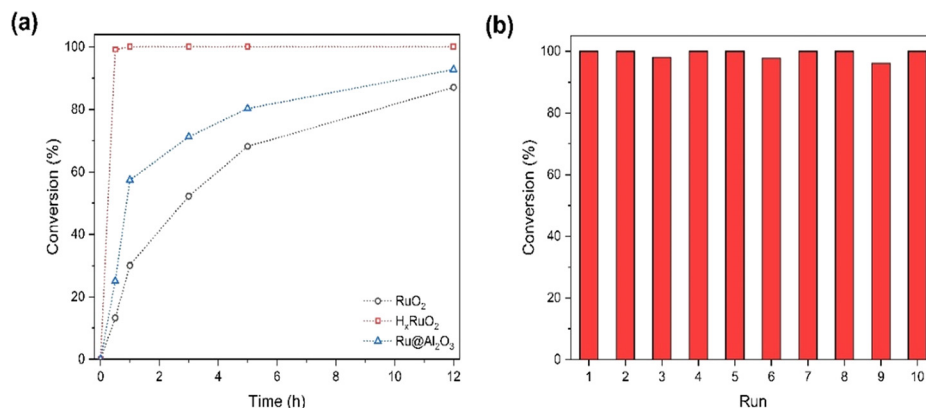
The reaction results are summarized in Table 1. When using the  $H_xRuO_2$  as a catalyst, complete conversion of toluene to methyl cyclohexane was achieved under 2 MPa of  $H_2$  at 50 °C within 1 h (Table 1, entry 1). Methyl cyclohexane was observed as the sole product, and no partial hydrogenation products such as methyl cyclohexene and methyl cyclohexadiene were identified. Performing the same

**Table 1** Hydrogenation of toluene to methylcyclohexane catalyzed by ruthenium-based catalysts

Entry <sup>a</sup>	Catalyst	Temperature [°C]	Pressure [MPa]	Time [h]	Conversion [%]
1	$H_xRuO_2$	50	2	1	>99
2	$RuO_2$	50	2	1	30.1
3	$Ru@Al_2O_3$ <sup>b</sup>	50	2	1	57.5
4	$H_xRuO_2$	25	4	2	>99
5	$RuO_2$	25	4	2	N.D.
6	$Ru@Al_2O_3$	25	4	2	15.3

<sup>a</sup> Reaction condition: batch reactor, toluene (1 mL, 9.4 mmol), catalyst (10 mg). <sup>b</sup> 5 wt% ruthenium on alumina; N.D.: not detected.





**Fig. 3** Catalytic performance in the hydrogenation of toluene. (a) Comparison of the conversion over reaction time using three different catalysts. Reaction conditions: toluene (1 mL, 9.4 mmol), catalyst (10 mg), 2 MPa H<sub>2</sub>, 50 °C. (b) Study on recyclability study of the H<sub>x</sub>RuO<sub>2</sub> catalyst. Reaction conditions: toluene (1 mL, 9.4 mmol), catalyst (10 mg), 4 MPa H<sub>2</sub>, room temperature, 2 h.

reaction in the presence of rutile RuO<sub>2</sub>, however, the yield of methyl cyclohexane decreased to 30% (Table 1, entry 2). The Ru@Al<sub>2</sub>O<sub>3</sub> catalyst exhibits only 57% conversion of toluene (Table 1, entry 3). Fig. 3a displays the conversion of toluene over the three catalysts as a function of time. We note that rapid hydrogen uptake occurs at the beginning of the reaction with the H<sub>x</sub>RuO<sub>2</sub> catalyst, as shown in Fig. 3a. The conversions using the RuO<sub>2</sub> and Ru@Al<sub>2</sub>O<sub>3</sub> catalysts increase with increasing reaction time, but full conversions were not reached even after 12 hours of reaction. This clearly suggests that H<sub>x</sub>RuO<sub>2</sub> has a standalone catalytic function, especially for hydrogenation reactions.

The effect of H<sub>2</sub> pressure on toluene hydrogenation was also examined. When 4 MPa of H<sub>2</sub> was applied, toluene hydrogenation in the presence of H<sub>x</sub>RuO<sub>2</sub> was completed even at room temperature within 2 h (Table 1, entry 4). In contrast, the RuO<sub>2</sub> catalyst did not show any activity and the Ru@Al<sub>2</sub>O<sub>3</sub> catalyst gave considerably lower conversion (Table 1, entries 5 and 6). This indicates that pressure plays a key role in promoting the activity of H<sub>x</sub>RuO<sub>2</sub>, while the pressure had little effect on the RuO<sub>2</sub> and Ru@Al<sub>2</sub>O<sub>3</sub> catalysts. The pressure-enhanced activity of H<sub>x</sub>RuO<sub>2</sub> might be ascribed to interstitial protons in the RuO<sub>2</sub> lattice. The protic hydrogen seems to be highly mobile and strongly reactive under high H<sub>2</sub> pressure. Chen *et al.* reported a novel state of hydrogen with extremely high mobility in hydrogenated Nb<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub>, which quickly reduces Cu<sup>2+</sup> ions into Cu<sup>0</sup> *via* proton transfer but has a very short lifetime.<sup>27</sup> On the other hand, protons in H<sub>x</sub>RuO<sub>2</sub> are mobile and also exhibit a high stability, as evidenced by the intact XRD pattern of H<sub>x</sub>RuO<sub>2</sub> after annealing at 150 °C at 2 MPa of H<sub>2</sub>. Next, we studied the stability of the H<sub>x</sub>RuO<sub>2</sub> catalyst because recycling used catalysts is an essential part of the economic evaluation of arene hydrogenation. Therefore, catalyst reuse experiments were conducted to prove the recyclability of H<sub>x</sub>RuO<sub>2</sub>. The catalytic activity of the used catalyst is shown in Fig. 3b. Complete conversion of toluene was evident even after ten cycles and any noticeable deactivation of the catalyst was not detected. In addition, no structural change was observed,



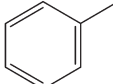
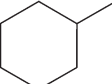
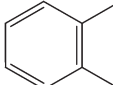
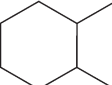
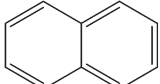
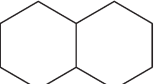
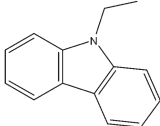
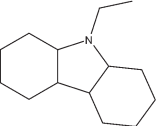
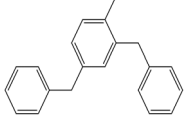
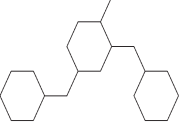
which was confirmed by powder XRD. The recycling results demonstrate that the H<sub>x</sub>RuO<sub>2</sub> catalyst retains high activity against repeated toluene hydrogenations and can be used in industrially relevant continuous processes. In contrast, the catalytic activity of rutile RuO<sub>2</sub> decreased with increasing cycles under the same conditions, mainly because RuO<sub>2</sub> is easily decomposed into Ru. This indicates that the presence of hydrogen in H<sub>x</sub>RuO<sub>2</sub> plays an important role in stabilizing the oxide framework.

The catalytic performance of Ru-based catalysts for converting toluene to methyl cyclohexane reported in the literature is summarized in Table S3† for comparison. The Ru catalysts supported on various materials exhibit superior activity in toluene hydrogenation, but temperatures higher than 100 °C are required for complete conversion (Table S3,† entries 1–6). Very recently, low temperature catalytic activity in aromatic hydrogenation has been identified using alkali-modified Ru–Na catalysts,<sup>28</sup> which was performed at 60 °C and 2 MPa of H<sub>2</sub> (Table S3,† entry 7). As seen in entry 8, H<sub>x</sub>RuO<sub>2</sub> showed similar hydrogenation activity at lower temperatures and pressures than the Ru–Na catalyst. By simply raising the H<sub>2</sub> pressure to 4 MPa, moreover, the hydrogenation of toluene is completed within 2 h even at 25 °C. (Table S3,† entry 9). Compared to previously known heterogeneous Ru-based catalysts, the H<sub>x</sub>RuO<sub>2</sub> catalyst shows better catalytic performance for toluene hydrogenation. It is worth mentioning that catalysts operating at low temperatures are important because hydrogenation is an exothermic reaction that can break C–C bonds.

To expand the scope of arene hydrogenation using the H<sub>x</sub>RuO<sub>2</sub> catalyst, we investigated the reactivity of various arene substrates in the absence of solvent. Table 2 shows the best results optimized for complete conversion of arenes into corresponding fully hydrogenated products. Like toluene hydrogenation, the conversion of benzene to cyclohexane proceeded smoothly at room temperature (Table 2, entry 1). However, for xylene, a full conversion was achieved at 60 °C (Table 2, entry 3). Benzene, toluene, and xylene, which are referred to as BTX in the petrochemical industry, were readily converted to the corresponding saturated hydrocarbons



Table 2 Hydrogenation of various arenes catalyzed by H<sub>x</sub>RuO<sub>2</sub>

Entry <sup>a</sup>	Substrate	Product	Temperature [°C]	Pressure [MPa]	Time [h]	Conversion [%]	Selectivity [%]
1			25	4	0.8	>99	>99
2			25	4	1	>99	>99
3			25	4	2	>99	>99
4 <sup>b</sup>			120	5	3	>99	>99
5 <sup>c</sup>			120	5	3	>99	>98 <sup>d</sup>
6 <sup>c</sup>			120	5	3	>99	>99 <sup>e</sup>

<sup>a</sup> Reaction condition: batch reaction, substrate (9.4 mmol), catalyst (20 mg), reaction mixture stirred at 600 r.p.m. <sup>b</sup> Substrate (5 mmol). <sup>c</sup> Substrate (1 mmol). <sup>d</sup> Selectivity to H12-NEC. <sup>e</sup> Selectivity to H18-DBT.

under mild conditions. Naphthalene, which is the simplest polycyclic aromatic hydrocarbon and is a crystalline solid, was converted to the fully hydrogenated product, decalin. Remarkably, decalin is formed as the sole product through a solid-state reaction (Table 2, entry 4).

*N*-Ethylcarbazole (H0-NEC) and dibenzyltoluene (H0-DBT) are also regarded as promising future LOHC materials.<sup>29,30</sup> The H<sub>x</sub>RuO<sub>2</sub> catalyst was investigated for the hydrogenation of the two LOHCs. *N*-ethyl-dodecahydro-carbazole (H12-NEC) along with partially hydrogenated products were obtained under 4 MPa of H<sub>2</sub> at 120 °C. However, increasing the pressure of H<sub>2</sub> to 5 MPa completely converts H0-NEC to H12-NEC within 3 h. Next, the hydrogenation of dibenzyltoluene (H0-DBT) was evaluated under similar reaction conditions. Complete conversion of H0-DBT to perhydro dibenzyltoluene (H18-DBT) was achieved at 120 °C and 5 MPa for 3 h. When the hydrogenation reactions of H0-NEC and H0-DBT were performed in the presence of the Ru@Al<sub>2</sub>O<sub>3</sub> catalyst, however, the yield of the desired products drastically decreased under identical conditions. Most of the hydrogenation reactions with Ru-based catalysts reported thus far have been investigated at temperatures higher than 150 °C to obtain higher yields ranging from 90 to 99%.

All these results show that H<sub>x</sub>RuO<sub>2</sub> is catalytically more active, especially for hydrogenation reactions of aromatic compounds than rutile RuO<sub>2</sub> and commercial Ru@Al<sub>2</sub>O<sub>3</sub> catalysts. Moreover, the catalytic reactions proceeded smoothly

in the absence of solvent and the H<sub>x</sub>RuO<sub>2</sub> is quite stable even under harsh reducing conditions. The solventless hydrogenation of various arenes using the H<sub>x</sub>RuO<sub>2</sub> catalyst might be attractive for industrial applications because neither solvent nor purification steps are required. In addition, the lack of additional steps reduces energy consumption and lowers capital investment. Therefore, it can be considered a more environmentally benign and cost-effective process.

### Chemoselective hydrogenation of nitroarenes to anilines

To determine whether H<sub>x</sub>RuO<sub>2</sub> could act as a chemoselective catalyst, we tested various nitroarenes that contained at least nitro and phenyl groups. They are challenging substrates because they have reducible moieties in addition to the nitro group. The resulting aniline and its derivatives are industrially important chemicals that are widely used as precursors for the manufacture of polymers, agrochemicals, and pharmaceuticals.<sup>31,32</sup> Noble metal catalysts are well known for the reduction of nitroarenes to anilines. Because of their high reactivity, they often lead to the formation of undesirable by-products such as hydroxylamine.<sup>33</sup> The desired selectivity might be achieved by an oxide-based H<sub>x</sub>RuO<sub>2</sub> catalyst.

Nitrobenzene was chosen as an initial model substrate to determine the optimal conditions for the hydrogenation reaction. The reaction was completed in a water-methanol solvent within 1 h at 60 °C under 0.5 MPa of H<sub>2</sub>. The H<sub>x</sub>RuO<sub>2</sub>



**Table 3** Hydrogenation of nitroarenes to anilines catalyzed by ruthenium-based catalysts

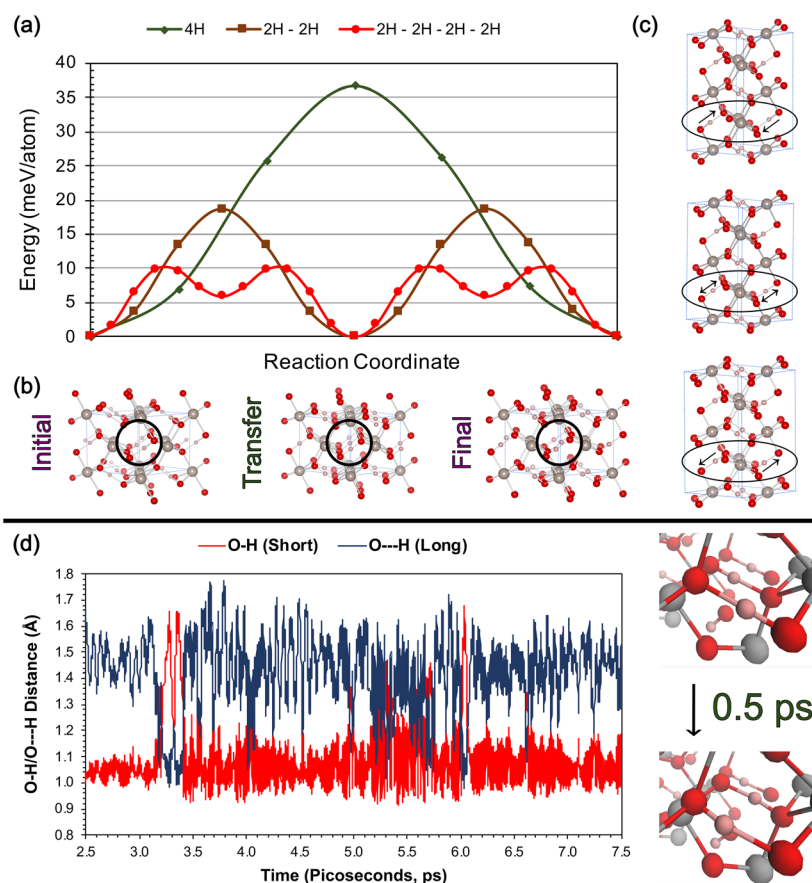
Entry <sup>a</sup>	Catalyst	Substrate	Temperature [°C]	Pressure [MPa]	Time [h]	Conversion [%]
1	H <sub>x</sub> RuO <sub>2</sub>	Nitrobenzene	60	0.5	1.0	>99
2	RuO <sub>2</sub>	Nitrobenzene	60	0.5	1.5	29.1
3	Ru@Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	Nitrobenzene	60	0.5	1.5	27.0
4	H <sub>x</sub> RuO <sub>2</sub>	<i>p</i> -Nitrophenol	40	0.5	1.0	>99
5	RuO <sub>2</sub>	<i>p</i> -Nitrophenol	40	0.5	1.0	9.5
6	Ru@Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	<i>p</i> -Nitrophenol	40	0.5	1.0	9.1

<sup>a</sup> Reaction condition: batch reactor, stirring bar, substrate (1 mmol), solvent = methanol/H<sub>2</sub>O (1 : 1) 2 mL, catalyst (10 mg). <sup>b</sup> 5 wt% ruthenium on alumina.

catalyst produces the desired aniline in excellent yield (>99%) with no by-products (Table 3, entry 1), clearly showing that H<sub>x</sub>RuO<sub>2</sub> is an active catalyst for the chemoselective reduction of the nitro group. On the other hand, when RuO<sub>2</sub> and Ru@Al<sub>2</sub>O<sub>3</sub> were used as catalysts under the same conditions, the yields dropped to less than 30% (Table 3, entries 2 and 3). Based on the optimized reaction conditions, 4-nitrophenol, which possesses a hydroxyl group *para* to the nitro group on the phenyl ring, was tested. The use of H<sub>x</sub>RuO<sub>2</sub> produced the

desired 4-aminophenol in a yield greater than 99% (Table 3, entry 4), whereas much lower yields were obtained with RuO<sub>2</sub> and Ru@Al<sub>2</sub>O<sub>3</sub> (Table 3, entries 5 and 6).

Next, the general scope of our H<sub>x</sub>RuO<sub>2</sub> catalyst was demonstrated in the reduction of functionalized nitroarenes. As shown in Table S4,<sup>†</sup> they afforded the corresponding anilines in excellent yields over 99%. A notable finding is that substrates having slightly bulky electron-donating groups (Table S4,<sup>†</sup> entries 3 and 4) as well as nitroarenes containing



**Fig. 4** Computational investigation of proton transfer energetics. (a) Comparison of simultaneous proton transfer (4H), concerted proton transfer (2H-2H), and concerted proton transfer in a  $1 \times 2 \times 1$  supercell (2H-2H-2H-2H) energies determined via Nudged Elastic Band (NEB) calculations. (b) Initial, midpoint, and final proton transfer structures for simultaneous proton transfer (4H). (c) Initial, midpoint, and final proton transfer structures for concerted proton transfer in a  $1 \times 2 \times 1$  supercell (2H-2H-2H-2H) with an emphasis placed on direction of proton motion. (d) O-H and O...H distances for a selected O-H...O bond during a FPMD simulation post-equilibration at 298 K in a  $2 \times 2 \times 2$  supercell, showing multiple proton transfers during the simulation. Inset highlights a proton that undergoes an O...H-O to O-H...O transfer after about 0.5 ps of the simulation.



electron-withdrawing elements (Table S4,† entries 5 and 6) were smoothly hydrogenated under mild conditions. All these results clearly show that  $H_xRuO_2$  not only outperforms rutile  $RuO_2$  and commercial  $Ru@Al_2O_3$  catalyst, but also acts as a catalyst for highly selective hydrogenations.

### Catalytic significance of interstitial hydrogen in $H_xRuO_2$

To determine whether the interstitial protons are key for the catalytic activity, we investigated the hydrogenation of benzene using deuterated  $D_xRuO_2$ . Catalytic hydrogenation of benzene was performed under the same conditions. Deuterated cyclohexane derivatives were identified from the reaction products by gas chromatography-mass spectrometer and  $^1H$  NMR, clearly showing a direct transfer of deuterium from  $D_xRuO_2$  to benzene. The deuterium vacancies in  $D_xRuO_2$  are replenished by dissociated H species. This suggests that interstitial protons within  $H_xRuO_2$  play a crucial role in accelerating hydrogenation reaction.

Werner and coworkers reported spectroscopic evidence for the coexistence of surface and bulk H species upon  $H_2$  dissociation over  $CeO_2$ , suggesting that the Ce–H species are reactive enough to participate in the hydrogenation reaction.<sup>34</sup> Like the  $H_2$ – $CeO_2$  interaction, the dissociation of  $H_2$  occurs on  $H_xRuO_2$ , producing dissociated H species. The H species diffuse over oxide surfaces and can easily jump from one site to another, which appears to be assisted by the presence of mobile protons in bulk  $H_xRuO_2$ . This proton-hopping process might be related to the Grotthuss mechanism.<sup>35</sup> The vacant interstitial sites appear to serve as highly efficient conduits for rapid proton-hopping leading to the exceptional catalytic activity of  $H_xRuO_2$ .

### Computational studies

To better understand the barriers involved in the proton transfer density functional theory (DFT) nudged elastic band (NEB) calculations<sup>36</sup> were carried out on the  $P2_1/c$   $RuO_2H$  phase (Fig. 4a). When all four of the hydrogen atoms within a single unit cell (4H) were transferred simultaneously a barrier of  $\sim 37$  meV per atom was obtained, with the initial, midpoint and final structures illustrated in Fig. 4b. A second stepwise 2H–2H mechanism was found wherein two hydrogens were initially transferred from O–H $\cdots$ O into O $\cdots$ H–O moieties, followed by an additional transfer of two hydrogens. This mechanism resulted in two barriers of 19 meV per atom each. Finally, a 2H–2H–2H–2H transfer mechanism in an  $RuO_2H$  supercell was found to possess an even smaller barrier, with intermediates that lay 6 meV per atom higher in energy than the ground state (Fig. 4c). The hydrogen atoms in the intermediates were found to lie slightly off center from the midpoint. Such a lowering of the barrier upon enlarging the cell used to model the structure suggests that the barrier would decrease further using larger supercells.

Further first-principles molecular dynamics (FPMD) simulations on a supercell of  $P2_1/c$   $RuO_2H$  showed that

hydrogen transfers occur spontaneously at room temperature. Selected O–H bond distances were plotted as a function of time (Fig. 4d) to analyze the proton dynamics. In a proton transfer event an O–H distance lengthened to 1.4–1.6 Å while at the same time an H $\cdots$ O distance shortened to  $\sim 1.1$  Å. Some protons that were transferred near the beginning of the FPMD run remained so during the full duration of the simulation, while others quickly returned to their respective short O–H bond lengths. The protons spent about 2.5% of the simulation time bonded to an oxygen atom that differed from the one in the starting geometry. Inclusion of anharmonic and quantum nuclear effects are likely to further enhance the degree of proton transfer. These computational studies suggest that the facile proton dynamics may be related to the remarkable catalytic activity of  $H_xRuO_2$ .

## Conclusions

In conclusion, we have developed a new ruthenium dioxide  $H_xRuO_2$  that adopts a monoclinic structure with interstitial protons.  $H_xRuO_2$  acts as a standalone catalyst, exhibits highly selective hydrogenation under mild conditions, and outperforms rutile  $RuO_2$  and commercial  $Ru@Al_2O_3$  catalysts. Furthermore,  $H_xRuO_2$  is recyclable and stable in both acidic and alkaline media. The mobile proton embedded in the oxide lattice plays an important role in stabilizing the distorted structure and maintains the hydrogen flux without diffusion limitation, substantially enhancing the catalytic properties through coupled proton–electron transfer. The discovery of  $H_xRuO_2$  and its excellent catalytic activity opens up new perspectives to explore H-bearing metal oxides that can serve as new exotic materials as well as hydrogenation catalysts.

## Experimental methods

### Synthesis of hydrogen-bearing ruthenium dioxide ( $H_xRuO_2$ )

In a 10 mL reaction vial, 0.30 g of polycrystalline  $RuO_2$  was mixed with 0.3 mL of deionized water. The reaction vial was placed into a 45 mL autoclave. The autoclave was purged twice with CO and then pressurized to 1.5 MPa CO at room temperature. The autoclave was heated to 200 °C and maintained for 6 hours at 200 °C. After completion of the reaction, the autoclave was cooled to room temperature. The resulting black solid was washed with toluene three times and dried under vacuum for 2 hours. The typical yield of  $H_xRuO_2$  based on the used  $RuO_2$  was about 94% (0.28 g).

### General procedure for catalytic hydrogenation

The catalytic hydrogenation was conducted in a 45 mL stainless autoclave. Typically, substrate was mixed with the  $H_xRuO_2$  catalyst (10 mg) in a 10 mL reaction vial equipped with a magnetic stirring bar. The reaction vial was placed into the autoclave. The autoclave was purged twice with  $H_2$  at room temperature, which was then pressurized with  $H_2$  to 0.5–8.0 MPa. The autoclave was maintained at 25–120 °C with



stirring for a given period of time. After completion of the reaction, the autoclave was cooled to room temperature. The products were analyzed by NMR. NMR data of the products are given in the ESI.†

### Computational details

Precise geometry optimizations, <sup>1</sup>H NMR chemical shifts, electronic density of states, band structure, first principles molecular dynamics (FPMD), and nudged elastic band (NEB) calculations were performed using density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) functional<sup>37</sup> as implemented in the Vienna *ab initio* simulation package (VASP).<sup>38,39</sup> A plane wave basis set with an energy cutoff of 600 eV was used along with projector-augmented wave (PAW) potentials<sup>40</sup> where the H 1s<sup>1</sup>, O 2s<sup>2</sup>2p<sup>4</sup>, and Ru 4d<sup>7</sup>5s<sup>1</sup> electrons were treated explicitly. Evolutionary structure searches were performed with the XTALOPT<sup>41</sup> algorithm. Further computational details are provided in the ESI.†

### Author contributions

H. J. Y. carried out the experiment and performed the characterization. M. R. and D. P. M. conducted the theoretical DFT simulations under the guidance of E. Z., M. K. and C. S. Y. contributed to the structure and Raman analysis. S. Y. L. conducted the Raman experiment under the guidance of H. C. and S. A. C. performed the solid state NMR spectroscopy. D. A. carried out the experiment at the beamline. N. H. H. conceived the project and directed the experiments. N. H. H. wrote the manuscript with contributions from all co-authors. All authors contributed to the discussion of the results.

### Conflicts of interest

There are no conflicts to declare.

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