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## 1. Introduction

Formaldehyde (HCHO) is one of the major indoor air pollutants, being harmful to human health,<sup>1–3</sup> and it has aroused wide concern especially in China. Therefore, it is of great interest to develop efficient methods and materials to eliminate indoor air HCHO. To date, numerous kinds of methods, including adsorption,<sup>4</sup> photocatalytic oxidation,<sup>5</sup> plasma techniques<sup>6</sup> and catalytic oxidation,<sup>7</sup> have been investigated for indoor HCHO abatement. Among them, catalytic oxidation is regarded as the most promising method

# Highly efficient Ru/CeO<sub>2</sub> catalysts for formaldehyde oxidation at low temperature and the mechanistic study<sup>†</sup>

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Formaldehyde (HCHO) elimination at low temperature is of great interest for indoor air purification. In this work, 1 wt% Ru supported on CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by an impregnation method and subsequently tested for the catalytic oxidation of HCHO at low temperature. The activity of the Ru/CeO<sub>2</sub> catalyst was significantly superior to the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst, achieving complete conversion of 130 ppm HCHO at 90 °C with a GHSV of 100 000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. Brunauer–Emmett–Teller (BET) measurements, X-ray powder diffraction (XRD), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray photoelectron spectroscopy (XPS) and H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) were carried out to characterize the physical and chemical properties of the catalysts. The results revealed that RuO<sub>x</sub> species, rather than Ru<sup>0</sup>, were directly responsible for the HCHO oxidation over Ru/CeO<sub>2</sub>, and the excellent performance of Ru/CeO<sub>2</sub> was mainly attributed to the strong interaction between Ru and CeO<sub>2</sub>, which induced a high dispersion and high redox capacity of RuO<sub>x</sub> species. The reaction mechanism of HCHO oxidation was also investigated using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS). It was shown that the HCHO oxidation over the Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts followed the same pathway of the direct formate oxidation (HCHO  $\rightarrow$  HCOO + OH  $\rightarrow$  H<sub>2</sub>O + CO<sub>2</sub>).

due to its high effectiveness without secondary pollution in achieving total conversion of HCHO.

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For decades, researchers have focused on catalysts including base metal oxides (Co, Cu, and Mn)8-11 and supported noble metal (Pt, Pd, Ag, Rh, and Au)<sup>12-30</sup> catalysts for HCHO oxidation. In general, base metal oxides require high temperatures to achieve complete oxidation of HCHO, whereas supported noble metal catalysts such as Na-Pt/TiO<sub>2</sub>, Na-Pd/TiO2 and Au/CeO2 catalysts can decompose HCHO into harmless CO2 and H2O at ambient temperature even at a high space velocity. However, the high cost has limited the wide application of Pt, Pd, and Au catalysts, thus accelerating the flourishing of studies on base metal oxides and also cheaper noble metal-based catalysts.<sup>10,20,27</sup> The effective operation temperature of metal-oxide catalysts, such as Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, CuHAP, MnO<sub>x</sub>-CeO<sub>2</sub>, etc., is higher than room temperature and generally around 70-160 °C.8-11 Therefore, the catalytic performance of base metal oxides still needs to be improved aiming for indoor HCHO elimination.

Ruthenium (Ru) is one of the noble metals and it is much less expensive compared with other metals such as Pt, Au and Pd. Ru-based catalysts have been extensively investigated for various kinds of oxidation processes, such as CO<sub>2</sub> methanation,<sup>31</sup> propane oxidation,<sup>32,33</sup> ammonia synthesis,<sup>34</sup> *etc.* In particular, Ru/CeO<sub>2</sub> catalysts have demonstrated

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Active reaction surface areas of the Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> samples (Table S1). HRTEM images of CeO<sub>2</sub> and Ru/CeO<sub>2</sub>-F and HAADF/STEM images of Ru/CeO<sub>2</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-F (bright field) (Fig. S1). The CO and CO<sub>2</sub> adsorption results of Ru/CeO<sub>2</sub>-F (Fig. S2). Stability testing results of Ru/CeO<sub>2</sub>-F at 85 °C (Fig. S3). Dynamic changes of *in situ* DRIFTS for Ru/CeO<sub>2</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-F (Fig. S4 and S5). Dynamic changes of *in situ* DRIFTS for the CO and CO<sub>2</sub> adsorption results of Ru/CeO<sub>2</sub>-F (Fig. S6 and S7). See DOI: 10.1039/d0cy01894e

excellent catalytic performances and exhibited advantages over other Ru-based catalysts in oxidation reactions, which have been mainly ascribed to the strong interaction between Ru species and  $CeO_2$ .<sup>32</sup> Formate (HCOO<sup>-</sup>) species are known as the key intermediate in HCHO oxidation, and the decomposition of formate is the rate-determining step for the reaction. As shown in a known "volcano plot for HCOO<sup>-</sup> decomposition", Ru metal is only less active than Pt but more active than other group VIII metals and the group IB metals.<sup>35</sup> It is suggested that the Ru-based catalysts should be also an efficient catalyst for HCHO oxidation; however, there have been no related reports to date. Hence, it is worth examining the performance of Ru-based catalysts in HCHO oxidation and revealing the related mechanism.

In this paper, we prepared Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts by an impregnation method, and tested the performances of the fresh and H<sub>2</sub> reduced samples for HCHO oxidation. The Ru/CeO2 catalyst demonstrated a much higher activity than the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst, and interestingly, H<sub>2</sub> reduction showed no influence on Ru/CeO2. Over fresh Ru/CeO2, 130 ppm HCHO could be completely decomposed into CO<sub>2</sub> and H<sub>2</sub>O at about 90 °C with a gas hourly space velocity of 100 000 mL  $g_{cat}^{-1}$  h<sup>-1</sup>. The catalysts were next characterized by XRD, BET, HAADF-STEM, XPS, H2-TPR and in situ DRIFTS methods. Based on the results, we revealed that  $RuO_x$  species, rather than Ru<sup>0</sup>, were the active sites for the HCHO oxidation; the high dispersion and high redox capacity of RuO<sub>x</sub> species induced by the strong interaction between Ru and the CeO2 support were responsible for the excellent catalytic performance of the Ru/CeO<sub>2</sub> catalyst.

## 2. Experimental

#### 2.1 Catalyst preparation

 $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was purchased from Aladdin, while the CeO<sub>2</sub> nanorod was prepared by a hydrothermal method.<sup>36</sup> Typically, 3 g of cerium nitrate and 15 g of NaOH were first dissolved in 30 ml and 50 ml of deionized water, respectively. After blending the two kinds of solution in a beaker, the mixture was stirred for 1 h and subsequently transferred into a Teflon-lined stainless steel autoclave at a temperature of 120 °C and it was maintained for 12 h. The fresh precipitates were thoroughly washed with deionized water and anhydrous ethanol to remove any possible ionic remnants. The solid obtained was dried at 60 °C in air overnight and calcined at 500 °C for 4 h in air.

Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts (1 wt% Ru/support) were prepared by an impregnation method at room temperature, using a ruthenium nitrite solution. After stirring for 1 h, excess water was removed in a rotary evaporator at 60 °C under vacuum until dryness. Then, the samples were dried at 100 °C overnight and calcined at 400 °C with a ramping rate of 5 °C min <sup>-1</sup> in static air for 2 h. The as-prepared samples were named Ru/CeO<sub>2</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-F. After pretreating Ru/ CeO<sub>2</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-F with H<sub>2</sub> at a rate of 30 mL min<sup>-1</sup> for 1 h at 300 °C, the samples were named Ru/CeO\_2-R and Ru/Al\_2O\_3-R.

#### 2.2 Catalyst characterization

X-ray powder diffraction (XRD) patterns of the samples were collected with an X'Pert PRO MPD X-ray powder diffractometer with Cu K $\alpha$  radiation operated at 40 kV and 40 mA. The patterns were measured over the  $2\theta$  range from 10° to 80° at a scan step of 0.02°.

The specific surface area and pore characterization of the catalysts were obtained at -196 °C over the whole range of relative pressures, using a Quantachrome Quadrasorb SI-MP analyzer. Before  $N_2$  physisorption, the catalysts were degassed at 300 °C for 3 h. The specific surface area of the samples was calculated by the Brunauer–Emmett–Teller (BET) method. The diameter and volume of pores were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a JEOL JEM-ARM 200F with a Cs-corrected probe operated at 200 kV. Typically, a drop of the nanoparticle solution was dispensed onto a 3 mm carbon-coated copper grid. Excess solution was removed using an absorbent paper, and the sample was dried at 80 °C.

X-ray photoelectron spectroscopy (XPS) was conducted using an AXIS Ultra system, with Al K $\alpha$  radiation (hv = 1486.6eV) with an X-ray anode operated at 225 W and 15 kV. The C 1s peak (284.8 eV) was used to calibrate the binding energy (BE) values.

 $H_2$ -temperature-programmed reduction ( $H_2$ -TPR) was carried out on a chemisorption analyzer (AutoChem 2920) equipped with a TCD. In the typical test, the samples were pretreated with 10% O<sub>2</sub>/He or 10% H<sub>2</sub>/Ar at 300 °C. The H<sub>2</sub>pretreated samples were then treated with 10% O<sub>2</sub>/He at 25 °C, 100 °C or 150 °C, respectively, and the treated samples were named Ru/support-R-O<sub>2</sub>-temperature. Thereafter, H<sub>2</sub>-TPR profiles were obtained by passing a flow of 10% H<sub>2</sub>/Ar at a rate of 50 mL min<sup>-1</sup> through the sample (weight of around 100 mg). The temperature was increased from 25 to 300 °C at a rate of 10 °C min<sup>-1</sup>, and the H<sub>2</sub> consumption was monitored using the TCD after the removal of produced H<sub>2</sub>O.

The CO pulse experiments were carried out on a chemisorption analyzer (AutoChem 2920) equipped with a TCD to identify the real active reaction surface area of Ru/ $CeO_2$  and Ru/Al<sub>2</sub>O<sub>3</sub>.<sup>37,38</sup> The details are shown in the ESI.†

#### 2.3 In situ DRIFTS study

In situ DRIFTS experiments were performed on a Thermo Fisher IS 50 spectrometer equipped with a smart collector and a liquid  $N_2$  cooled MCT detector. The flow of the feed gas mixture was controlled using mass flow meters. All the spectra were measured with a resolution of 4 cm<sup>-1</sup> and an accumulation of 32 scans. A background spectrum was subtracted from each spectrum.

#### 2.4 Activity test for formaldehyde oxidation

The activity tests for the catalytic oxidation of HCHO over the catalysts (60 mg) were performed in a fixed-bed quartz flow reactor with a gas mixture containing 130 ppm HCHO, 20%  $O_2$ , 35% relative humidity (RH) and He balance at a total flow rate of 100 cm<sup>3</sup> min<sup>-1</sup> (GHSV = 100 000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). Water vapor was generated by flowing helium through a water bubbler at 25 °C, and the relative humidity in the reaction atmosphere was controlled by adjusting the flow rate of the purging helium and measured using a hygrometer. Gaseous HCHO was obtained by flowing helium through a paraformaldehyde container in a water bath, and the concentration of inlet HCHO was controlled by adjusting the inlet and outlet gases and the carbon balance calculation were performed as shown in our previous study.<sup>23</sup>

### Results and discussion

#### 3.1 Activity test

Fig. 1 presents the HCHO conversions as a function of temperature over the CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> samples before and after H<sub>2</sub> treatment. The pure Al<sub>2</sub>O<sub>3</sub> support exhibited no activity for HCHO oxidation in the testing temperature range of 25 °C to 160 °C, and the CeO<sub>2</sub> support also showed poor activity with only 40% HCHO conversion at 160 °C. After loading 1% Ru, the performances of Ru/CeO<sub>2</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-F were clearly improved. Ru/CeO<sub>2</sub>-F exhibited a much higher activity than Ru/Al<sub>2</sub>O<sub>3</sub>-F at each testing temperature point, and reaching 100% HCHO



**Fig. 1** HCHO conversions over the CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ru/CeO<sub>2</sub> and Ru/ Al<sub>2</sub>O<sub>3</sub> samples. F: fresh sample; R: H<sub>2</sub> reduced sample. Reaction conditions: 130 ppm HCHO, 20% O<sub>2</sub>, 35% RH, He balance, GHSV = 100 000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (inset: results of stability testing performed at 85 °C under the conditions of 130 ppm HCHO and GHSV = 100 000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>).

conversion at around 90 °C. In contrast, HCHO could not be entirely decomposed over  $Ru/Al_2O_3$ -F until 160 °C. We have also carried out a long-time stability testing over  $Ru/CeO_2$ -F at 85 °C, and the results (Fig. 1(inset)) show that about 75% HCHO conversion could be maintained for 24 h.

After  $H_2$  pretreatment, the activity of the Ru/Al<sub>2</sub>O<sub>3</sub>-R catalyst was only slightly improved, and Ru/CeO<sub>2</sub>-R showed almost the same performance as the Ru/CeO<sub>2</sub>-F catalyst for HCHO oxidation. These findings indicate that  $H_2$  reduction has a limited effect on the Ru-based catalysts, which is much different from the  $H_2$  reduction effect on the supported Pt, Pd and Ir catalysts, where  $H_2$  pretreatment is always necessary for their excellent performances in ambient HCHO oxidation.<sup>13,21,22,39</sup>

#### 3.2 Physical characterization

The specific surface areas (BET), average pore diameters, and total pore volumes of the samples were measured and the results are presented in Table 1. The  $Al_2O_3$  support exhibited a high specific surface area (167 m<sup>2</sup> g<sup>-1</sup>), while the specific surface area of CeO<sub>2</sub> was 90 m<sup>2</sup> g<sup>-1</sup>. The supported Ru samples presented similar physical properties to the CeO<sub>2</sub> or  $Al_2O_3$  support. The Ru/CeO<sub>2</sub> catalyst had lower surface areas than Ru/Al<sub>2</sub>O<sub>3</sub>, but presented better performance for HCHO oxidation, indicating that the physical properties have limited influence on the catalytic activity of Ru-based catalysts.

XRD measurements were next carried out to investigate the crystallographic structures of the samples, and the results are shown in Fig. 2. The XRD patterns of the Ru/CeO2-F and Ru/CeO2-R samples only exhibited the diffraction peaks of the CeO<sub>2</sub> support and no peaks ascribed to Ru species (Ru<sup>0</sup>, RuO<sub>2</sub>, and RuO<sub>3</sub>) were observed, indicating that the Ru species were well dispersed on the CeO<sub>2</sub> support. When Ru was loaded on the  $Al_2O_3$  support, the (110), (101) and (211) reflections of crystalline RuO<sub>2</sub> (PDF no. 43-1027), corresponding to 28.0, 35.1 and 54.3° (2 $\theta$ ), respectively, were detected on the Ru/Al<sub>2</sub>O<sub>3</sub>-F catalyst. After H<sub>2</sub> treatment, the peaks of RuO<sub>2</sub> disappeared and the (100), (002) and (101) reflections of metallic Ru (PDF no. 06-0663), corresponding to 38.4, 42.2 and 44.0° ( $2\theta$ ), respectively, appeared on the Ru/ Al<sub>2</sub>O<sub>3</sub>-R catalyst, indicating that the RuO<sub>2</sub> species were reduced to metallic Ru and the Ru particle size decreased after H<sub>2</sub> treatment. However, due to the overlap between Ru<sup>0</sup>

 $\label{eq:table_$ 

Samples	$S_{\text{BET}}$ $(\text{m}^2 \text{g}^{-1})$	Pore volume $(ml g^{-1})$	Pore diameter (nm)
CeO <sub>2</sub>	90	0.4	19.9
Ru/CeO2-F	94	0.4	16.2
Ru/CeO2-R	95	0.4	15.1
$Al_2O_3$	167	0.9	21.8
Ru/Al <sub>2</sub> O <sub>3</sub> -F	162	0.9	19.8
Ru/Al <sub>2</sub> O <sub>3</sub> -R	161	0.9	19.6
Ru/Al <sub>2</sub> O <sub>3</sub> -F Ru/Al <sub>2</sub> O <sub>3</sub> -R	162 161	0.9 0.9	19.8 19.6



Fig. 2 XRD patterns of the CeO\_2, Al\_2O\_3, Ru/CeO\_2 and Ru/Al\_2O\_3 samples.

peaks and  $Al_2O_3$  peaks, the diffraction peaks of  $Ru^0$  were inconspicuous on the  $Ru/Al_2O_3$ -R catalyst. The XRD results revealed that there was a much larger Ru particle size on the  $Ru/Al_2O_3$  catalyst compared with that on the  $Ru/CeO_2$  catalyst.

Fig. 3 and 4 show the HAADF-STEM pictures (dark field) and EDS elemental mapping images of the Ru/CeO<sub>2</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-F catalysts (for the bright field results and HRTEM results, see the ESI,† Fig. S1). As shown in Fig. 3a, the Ru species was not observed on the Ru/CeO<sub>2</sub>-F catalyst due to



Fig. 3 HAADF-STEM images of Ru/CeO<sub>2</sub>-F (a and b, dark field) (inset: the dislocation analysis result of the red square region); HAADF-STEM EDS elemental mapping images of Ru/CeO<sub>2</sub>-F (c). For the bright field results and HRTEM images, see the ESI,† Fig. S1.



Fig. 4 HAADF-STEM images of Ru/Al<sub>2</sub>O<sub>3</sub>-F (a and b, dark field); HAADF-STEM EDS elemental mapping images of Ru/Al<sub>2</sub>O<sub>3</sub>-F (c). For the bright field results, see the ESI,† Fig. S1.

the low contrast of Ru and Ce, while EDS elemental analysis (Fig. 3c) clearly showed the presence of Ru species with a uniform small particle size, indicating that Ru was highly dispersed on CeO2. In addition, Ru/CeO2-F exhibited abundant "dark pits", indicating the rough surface of  $CeO_{2}$ ,<sup>40</sup> and the dislocation analysis result (Fig. 3b) revealed the presence of dislocations on CeO<sub>2</sub>. Most defects are sites where electrons and holes recombine with special efficiency and are useful in improving the properties of catalysts.<sup>41</sup> Therefore, the special defect structure of the CeO<sub>2</sub> support provides active sites and it is favorable for the presence of oxygen vacancies and surface oxygen species on the catalyst. As shown in Fig. 4, remarkable agglomerations of Ru species were observed on the Ru/Al2O3-F catalyst. The Ru particles displayed a wider distribution on the Ru/Al2O3-F catalyst with dominating large particles (particle size of about 20 nm). The results of HAADF-STEM are consistent with the XRD results, revealing that Ru was steadily anchored on the CeO<sub>2</sub> surface, resulting in a high dispersion and small particle size of Ru species, and the presence of defects on the CeO<sub>2</sub> support also contributed to the activity of the Ru/ CeO2 catalyst. The active surface area of the Ru species over Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> was measured by the CO pulse experiments. It is shown that the high dispersion of Ru on CeO<sub>2</sub> led to a much higher active surface area of Ru/CeO<sub>2</sub> than that of  $Ru/Al_2O_3$  (Table S1<sup>†</sup>).

#### 3.3 XPS analysis

XPS measurements were next carried out to investigate the electronic state of surface Ru species. Fig. 5 shows the Ru 3d XPS spectra of the Ru/CeO2 and Ru/Al2O3 catalysts. Considering the overlap between the Ru 3d<sub>3/2</sub> peak and the C 1s peak at about 284.4 eV, the Ru 3d<sub>5/2</sub> peak at about 280 eV was employed to analyze the chemical state of surface Ru. Ru/CeO2-F showed two peaks at binding energies of 281.5 eV and 282.7 eV, which were assigned to Ru<sup>4+</sup> species and Ru<sup>6+</sup> species, <sup>31,42-44</sup> respectively, indicating that Ru on CeO<sub>2</sub> was mainly in the oxidation state. Over the Ru/CeO2-R sample, the peaks of Ru were located at 281.2 eV and 282.7 eV, showing that Ru was still in the oxidation state, and the slight shift of the Ru<sup>4+</sup> peak from 281.5 eV to 281.2 eV was mainly due to the slight increase of the electron density in the RuO<sub>r</sub> species after H<sub>2</sub> pretreatment. Hence, we believe that Ru species have a high redox capacity on the CeO<sub>2</sub> support, and the metallic Ru species formed by H<sub>2</sub> treatment could be easily oxidized back to RuOr species after being exposed to ambient air before the XPS measurement.

For the Ru/Al<sub>2</sub>O<sub>3</sub>-F sample, the peaks at 280.7 eV and 281.9 eV were observed and attributed to Ru4+ species and Ru6+ species, respectively. After H<sub>2</sub> treatment, two peaks of the RuO<sub>x</sub> species disappeared, and a single peak at 280.2 eV due to the metallic Ru species was detected on Ru/Al<sub>2</sub>O<sub>3</sub>-R.<sup>31,42-45</sup> It is suggested that the Ru oxides on Al2O3 were reduced into metallic Ru by H<sub>2</sub>, but the metallic Ru could not be easily oxidized back to RuOx species after being exposed to ambient air. Moreover, it is noted that the peaks of the Ru species on the Ru/Al<sub>2</sub>O<sub>3</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-R samples were very weak, indicating the poor dispersion and larger particle size of the Ru species on Al<sub>2</sub>O<sub>3</sub>,<sup>46</sup> which is consistent with the XRD and HAADF-STEM results. The XPS results suggest that the interaction between Ru and  $CeO_2$  was much stronger than that between Ru and  $Al_2O_3$ , contributing to the small size, high dispersion and high redox capacity of the Ru species on the CeO2 support.

Fig. 6 shows the O 1s XPS spectra of the Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. The peaks at 529.2–530.8 eV and 531.0–532.3 eV were assigned to lattice oxygen ( $O_{latt}$ ) and surface oxygen



Fig. 5 Ru 3d XPS results of the Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts.





 $(O_{surf})$ , respectively.<sup>26,32</sup> The  $O_{surf}/(O_{latt} + O_{surf})$  values of the Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> samples were calculated by the analysis of the integrated peak area, and the results are shown in Fig. 6. The ratios of  $O_{surf}/(O_{latt} + O_{surf})$  on the Ru/CeO<sub>2</sub> samples were much higher than those on Ru/Al<sub>2</sub>O<sub>3</sub>, revealing that the high oxygen storage capacity of CeO<sub>2</sub> promoted the content of surface oxygen on the catalyst, thus enhancing the oxygen activation capacity of the Ru/CeO<sub>2</sub> catalyst.

Fig. 7 shows the Ce 3d XPS results of the CeO<sub>2</sub> and Ru/CeO<sub>2</sub> samples. It is known that Ce<sup>3+</sup> is indicative of the presence of oxygen vacancies produced by the transformation of Ce<sup>4+</sup> into Ce<sup>3+</sup>, 4Ce<sup>4+</sup> + O<sup>2-</sup>  $\rightarrow$  2Ce<sup>4+</sup> + 2Ce<sup>3+</sup> +  $\Upsilon$  + 0.5 O<sub>2</sub> (where  $\Upsilon$  represents an empty position).<sup>36,40</sup> As shown in Fig. 7, the surface concentrations of Ce<sup>3+</sup> as a percent of the total Ce on CeO<sub>2</sub>, Ru/CeO<sub>2</sub>-F and Ru/CeO<sub>2</sub>-R were 17.3%, 18.4%, and 18.4%, respectively, indicating that the loading of Ru increased the concentration of oxygen vacancies on the Ru/CeO<sub>2</sub> catalyst, and was therefore beneficial to the O<sub>2</sub> activation.

#### 3.4 H<sub>2</sub>-TPR experiments

 $\rm H_2\text{-}TPR$  experiments were next conducted to study the reducibility of the catalysts, and the TPR profiles of the Ru/



Fig. 7 Ce 3d XPS results of the  $CeO_2$  and  $Ru/CeO_2$  samples.

CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts are shown in Fig. 8. As shown in Fig. 8a, no reduction peak was observed on pure CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the examined temperature range (25–300 °C). The TPR pattern of the Ru/CeO<sub>2</sub>-F sample shows three reduction peaks at around 62 °C, 82 °C and 115 °C. The peak located at 62 °C was mainly ascribed to the reduction of surface adsorbed oxygen, and the peaks at 82 °C and 115 °C were due to the reduction of the RuO<sub>x</sub> species interacting strongly and weakly with the CeO<sub>2</sub> surface,<sup>31,47–49</sup> respectively. Different from Ru/CeO<sub>2</sub>-F, Ru/Al<sub>2</sub>O<sub>3</sub>-F showed two peaks at around 113 °C and 159 °C, which were ascribed to the reduction of the RuO<sub>x</sub> species supported on Al<sub>2</sub>O<sub>3</sub>.

H<sub>2</sub>-TPR test was then performed on the Ru/support-R and O<sub>2</sub>-treated samples, and the results are presented in Fig. 8b. Ru/CeO<sub>2</sub>-R exhibited one weak reduction peak at 70 °C due to the reduction of adsorbed oxygen. The Ru/CeO<sub>2</sub>-R-O<sub>2</sub>-temperature samples exhibited two reduction peaks at around 70 °C and 82 °C, ascribed to the reduction of adsorbed oxygen and RuO<sub>x</sub> species interacting strongly with the CeO<sub>2</sub> surface, respectively. The presence of abundant active oxygen species on the Ru/CeO<sub>2</sub>-R-O<sub>2</sub>-temperature samples demonstrated that the Ru species possessed outstanding redox capacity on the



Fig. 8  $H_2$ -TPR profiles of (a) the fresh samples and supports and (b) the Ru/support-R and Ru/support-R-O<sub>2</sub>-temperature samples.

CeO<sub>2</sub> support even at room temperature, and the metallic Ru on the Ru/CeO2-R catalyst could be easily oxidized back to RuO<sub>x</sub> species after being exposed to ambient air, which is consistent with the XPS result. Ru/Al<sub>2</sub>O<sub>3</sub>-R exhibited no reduction peak, indicating that there was no surface oxygen species and RuO<sub>x</sub> species on Ru/Al<sub>2</sub>O<sub>3</sub>-R. As for the Ru/ Al<sub>2</sub>O<sub>3</sub>-R-O<sub>2</sub>-temperature samples, only Ru/Al<sub>2</sub>O<sub>3</sub>-R-O<sub>2</sub>-150 showed one peak at 121 °C, which is also related to the reduction of RuO<sub>x</sub> species, while no reduction peak was observed on other samples. These results indicate that metallic Ru on the Ru/Al2O3-R catalyst could not be oxidized at 25 °C and 100 °C, demonstrating the poor redox capacity of the Ru species on Al<sub>2</sub>O<sub>3</sub>. Combining the results of XPS and H<sub>2</sub>-TPR, the abundant surface oxygen species on the Ru/CeO<sub>2</sub> catalyst revealed the high redox capacity of the catalyst. Hence, we further confirmed that the strong interaction between Ru and CeO<sub>2</sub> promoted the dispersion and redox capacity of the supported Ru species, which is the main factor affecting the catalytic activity for HCHO oxidation.

#### 3.5 In situ DRIFTS study

The reaction mechanism of HCHO oxidation over the Ru/ CeO<sub>2</sub>-F and Ru/Al<sub>2</sub>O<sub>3</sub>-F catalysts was next investigated by using *in situ* DRIFTS at 85 °C and 160 °C, respectively. As shown in Fig. 9, when the Ru/CeO<sub>2</sub>-F catalyst was exposed to a flow of He + HCHO + O<sub>2</sub> + H<sub>2</sub>O for 60 min, the bands at 1375, 1562, 1596, 1845, 2717, 2845, 2932, 3630 and 3685 appeared. According to previous studies, <sup>13,14,17,27,39</sup> we ascribed the bands at 1375, 1562 and 1596 cm<sup>-1</sup> to the  $v(COO^-)$  and those at 2717, 2845, and 2932 cm<sup>-1</sup> to the v(CH) of the formate species. Meanwhile, two negative peaks of surface hydroxyl



**Fig. 9** In situ DRIFTS over Ru/CeO<sub>2</sub>-F after a flow of He + HCHO + O<sub>2</sub> + H<sub>2</sub>O for 60 min followed by He purging for 60 min, then O<sub>2</sub> purging for 30 min and finally He + O<sub>2</sub> + H<sub>2</sub>O for 30 min at 85 °C. For the dynamic time sequence of the DRIFTS spectra, see the ESI,† Fig. S4. Reaction conditions: HCHO: 130 ppm, O<sub>2</sub>: 20%, RH: 35%, He balance, total flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>.



**Fig. 10** In situ DRIFTS over Ru/Al<sub>2</sub>O<sub>3</sub>-F after a flow of He + HCHO +  $O_2$  + H<sub>2</sub>O for 60 min followed by He purging for 60 min, then  $O_2$  purging for 30 min and finally He +  $O_2$  + H<sub>2</sub>O for 30 min at 160 °C. For the dynamic time sequence of the DRIFTS spectra, see the ESI,† Fig. S5. Reaction conditions: HCHO: 130 ppm,  $O_2$ : 20%, RH: 35%, He balance, total flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>.

(OH) species at 3630 and 3685 cm<sup>-1</sup> were observed on the catalyst surface, suggesting that the formation of surface HCOO<sup>-</sup> consumed some OH species. With He purging and O<sub>2</sub> purging, the intensities of the HCOO<sup>-</sup> peaks slightly dropped. After exposing the catalyst to a flow of He +  $O_2$  +  $H_2O$ , the HCOO<sup>-</sup> species completely disappeared from the surface in 30 min, indicating that the HCHO oxidation over Ru/CeO2-F mainly follows the direct oxidation mechanism (HCHO  $\rightarrow$ HCOO + OH  $\rightarrow$  H<sub>2</sub>O + CO<sub>2</sub>).<sup>13</sup> Interestingly, we observed a new band at 1845 cm<sup>-1</sup> during the process over Ru/CeO<sub>2</sub>-F, which has not been reported in the previous studies on HCHO catalytic oxidation.13,14,17,21,27,39 We next carried out the CO and CO2 adsorption on Ru/CeO2-F to study the assignment of the band at 1845 cm<sup>-1</sup>, and the results are shown in Fig. S2.† When Ru/CeO2-F was exposed to a flow of CO + He and  $CO_2 + He$ , bands at around 1845 cm<sup>-1</sup> also appeared, indicating that this band should be related to the carbonate species. Since this species had almost no changes during the process, it should be a spectator species for HCHO oxidation over Ru/CeO2-F.

The same *in situ* DRIFTS experiments were also performed for the Ru/Al<sub>2</sub>O<sub>3</sub>-F catalyst, and the spectra in the steady state are presented in Fig. 10. After exposing the catalyst to a flow of He + HCHO + O<sub>2</sub> + H<sub>2</sub>O for 60 min, the formate species (1395 and 1596 cm<sup>-1</sup> for  $\nu$ (COO<sup>-</sup>) and 2742, 2893, and 3000 cm<sup>-1</sup> for  $\nu$ (CH)) and carbonate (1852 cm<sup>-1</sup>) were formed. The bands of the formate species had almost no change after He purging for 60 min and O<sub>2</sub> purging for 30 min, and also the bands did not disappear after exposing to the flow of He + O<sub>2</sub> + H<sub>2</sub>O in 30 min. The band at 1851 cm<sup>-1</sup> also appeared but its intensity was much weaker than that on the Ru/CeO<sub>2</sub>-F catalyst, indicating that the carbonate species was very easily formed on the Ru/ CeO<sub>2</sub>-F catalyst. Considering the XPS and H<sub>2</sub>-TPR results, the Ru/CeO<sub>2</sub> catalyst possessed more abundant surface oxygen species than the  $Ru/Al_2O_3$  catalyst, which was favorable for the formation of the carbonate.<sup>50</sup>

The carbonate species at 1845 cm<sup>-1</sup> was considered as a spectator species, which should have a limited effect on the activity of the Ru/CeO<sub>2</sub>-F catalyst. We next added CO<sub>2</sub> to the gas mixture during the stability test of the Ru/CeO<sub>2</sub>-F sample to investigate the influence of the carbonate on the performance at 85 °C. As shown in Fig. S3,† the stability of Ru/CeO<sub>2</sub>-F and Ru/CeO<sub>2</sub>-F-CO<sub>2</sub> was similar, demonstrating that the presence of CO<sub>2</sub> did not affect the activity of the Ru/CeO<sub>2</sub>-F catalyst. Thus, we further confirmed that the carbonate at about 1845 cm<sup>-1</sup> was a spectator species.

Our previous studies showed that the adsorbed  $H_2O$  on Pt and Pd catalysts could be activated to form surface OH groups participating in the direct oxidation of formate.<sup>13,21</sup> In this study, we observed that the presence of  $H_2O$  could also enhance the activity of the Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. Based on these results, we concluded that HCHO oxidation over the Ru/CeO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts followed the same mechanism of HCHO  $\rightarrow$  HCOO + OH  $\rightarrow$  H<sub>2</sub>O + CO<sub>2</sub>.

## 4. Conclusions

In summary, the Ru/CeO2 and Ru/Al2O3 catalysts were prepared by an impregnation method, and the Ru/CeO<sub>2</sub> catalysts exhibited excellent catalytic performance, achieving complete HCHO conversion at around 90 °C. The CeO2 and Al<sub>2</sub>O<sub>3</sub> supports had different interactions with Ru, which affected the Ru dispersion, particle size and oxygen activation capacity, consequently influencing the catalytic activity. CeO<sub>2</sub> was found to be a more suitable support for Ru species to catalyze the HCHO oxidation at low temperature. The strong interaction between Ru and CeO2 induced the high dispersion, small particle size and high redox capacity of the Ru species on the CeO<sub>2</sub> support, resulting in a high capacity of Ru/CeO2 on O2 activation, and therefore beneficial to HCHO oxidation. Despite the considerable distinction in activities between Ru/CeO2 and Ru/Al2O3, the reaction mechanism of the HCHO oxidation followed the same pathway of direct formate oxidation (HCHO → HCOO + OH  $\rightarrow$  H<sub>2</sub>O + CO<sub>2</sub>).

## Conflicts of interest

There are no conflicts to declare.

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