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### Tuning the structure and catalytic activity of Ru nanoparticle catalysts by single 3d transitionmetal atoms in Ru<sub>12</sub>-metalloporphyrin precursors<sup>†</sup>

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Ru nanoparticle catalysts were prepared from Ru<sub>12</sub>-metalloporphyrin complex precursors containing 3d transition-metal atoms attached to SiO<sub>2</sub> surfaces. The single 3d metal atoms at the central position of the Ru<sub>12</sub>-metalloporphyrin complex precursors exerted a significant influence on the structures and hydrogenation performance of the Ru nanoparticles on the SiO<sub>2</sub> surfaces. The Ru<sub>12</sub>-Cu-porphyrin complex afforded positively charged Ru nanoparticles, which would provide high activity toward aromatic hydrogenation.

Tuning the catalytic performance of noble-metal nanoparticles/ nanoclusters by the addition of second (or even third) transition metals/metal oxides has attracted considerable attention in various fields of catalysis.<sup>1–5</sup> The combination of noble metals such as Pt, Au, Ru, Rh, and Pd with 3d transition metals such as Fe, Co, Ni, and Cu can lead to differences in catalytic performance compared with nanoparticles based on a single noble metal.<sup>6-12</sup> For example, the presence of 3d transition metals (M) in the core of Pt-M bimetallic nanoparticles afforded a higher activity for the oxygen reduction reaction in polymer electrode membrane fuel cells compared to monometallic Pt nanoparticles.<sup>6,7</sup> Furthermore, alloying of Pd nanoparticles with Ni atoms reduced the onset temperature for CO oxidation compared with monometallic Pd nanoparticles,<sup>8</sup> while the addition of Cu to Pd nanoparticles increased the activity and selectivity on the hydrogenation of CO<sub>2</sub> to ethanol.<sup>9</sup> The addition of Fe atoms to Ru nanoparticles altered the

selectivity during the reduction of unsaturated functional groups (C=C, C=O, and aromatic rings),<sup>10</sup> and the addition of Fe atoms to Pt nanoparticles increased the turnover frequency of ethylene/cyclohexene hydrogenation.<sup>11</sup> Using a bi- or trimetallic metal complex is a promising way to prepare bi- or trimetallic nanoparticles that exhibit unique catalytic activity and selectivity (e.g. Ru<sub>12</sub>Cu<sub>4</sub> nanoclusters for the hydrogenation of hex-1-ene, and Ru5-PtSn nanoparticles for the hydrogenation of dimethyl terephthalate).12,13 Co-loading of noble-metal nanoparticles with transition-metal oxides was also reported to lead to unusual catalytic behavior in terms of both activity and selectivity.<sup>14-17</sup> For instance, the boundary between  $FeO_x$  and Pt nanoparticles enhanced the reactivity during low-temperature CO oxidation.<sup>14</sup> However, there have been few reports to date concerning the influence of additional 3d transition metals/metal oxides on the structure and catalytic performance of noble-metal nanoclusters/nanoparticles, especially for those obtained from identical precursor structures.

Herein, we report that the structure of Ru nanoparticles on  $SiO_2$  is greatly affected by the presence of a single 3d metal atom in a precursor, namely  $Ru_{12}$ -metalloporphyrin complex, resulting in changes in the catalytic hydrogenation performance. The  $Ru_{12}$ -metalloporphyrin complexes (**1-Ru\_{12}M**) (M = Ni, Cu, Zn) were freshly prepared and attached to  $SiO_2$ . The reduction of the attached precursors afforded Ru nanoparticles with different degrees of oxidation in Ru species and hydrogenation activities depending on the 3d transition metal in the  $Ru_{12}$ -metalloporphyrin precursor.

Ru nanoparticles on SiO<sub>2</sub> were prepared in a stepwise manner as shown in Scheme 1, involving the grafting of an  $Ru_{12}$ -M–porphyrin complex (**1-Ru\_{12}M**) to a pyridine-functionalized SiO<sub>2</sub> surface (**A**) to afford **B-Ru\_{12}M** (step (a)), the stacking of SiO<sub>2</sub>-matrix overlayers around the grafted  $Ru_{12}$ -metalloporphyrin precursor to generate **C-Ru\_{12}M** (step (b)), and the reduction of the  $Ru_{12}$ -metalloporphyrin complex at 873 K to obtain Ru nanoparticles **D-RuM** (step (c)). Details of the synthetic procedures are presented in the ESI.†

In step (a), the pyridine moieties anchored on  $SiO_2$  in A (0.27 nm<sup>-2</sup>) were reacted with the transition-metal site at the

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Synthesis and characterization of **1-Ru<sub>12</sub>M**, preparation and characterization of **B-Ru<sub>12</sub>M**, **C-Ru<sub>12</sub>M**, and **D-RuM**, Ru/Cu/Ni/Zn K-edge XAFS, HAASF-STEM, XRD, and XPS data, and catalytic reaction results. See DOI: 10.1039/c7cc09862f



Scheme 1 Preparation of Ru nanoparticle-metal oxide catalysts on  $SiO_2$  surfaces from  $Ru_{12}$ -M-porphyrin complexes (1- $Ru_{12}$ M), and possible schematic representations of the surface structures of **D-RuCu** and **D-RuNi** as indicated by the surface analysis.

center of the porphyrin moiety of  $1-Ru_{12}M$ .<sup>18</sup> The resulting surface density of  $1-Ru_{12}M$  on SiO<sub>2</sub> was estimated to be 0.02 nm<sup>-2</sup> (see the ESI†). The loading of Ru was observed to be  $1.2 \pm 0.2$  wt% from X-ray fluorescence (XRF; Table S1, ESI†), which is comparable to the calculated value of 1.2 wt%.

Then, in step (b),  $Si(OCH_3)_4$  vapor was deposited onto the SiO<sub>2</sub> surface containing 1-Ru<sub>12</sub>M (B-Ru<sub>12</sub>M) and hydrolyzed to afford SiO<sub>2</sub>-matrix overlayers. (The average height of the SiO2-matrix overlayers was calculated to be 1 nm from the weight gain and the assumption that the SiO<sub>2</sub>-matrix overlayers have a quartz structure.)<sup>19–21</sup> The loading of Ru was dropped to around 0.68-0.70 wt% (Table S1, ESI<sup>+</sup>), suggested by the weight gain of the SiO2-matrix overlayers. The coordination structures of the supported Ru12-metalloporphyrin precursors were investigated by diffuse reflectance (DR)-ultraviolet/visible (UV/vis) spectroscopy and extended X-ray absorption fine structure (EXAFS). The DR-UV/vis spectra of B-Ru12Cu and C-Ru12Cu were similar to that of 1-Ru<sub>12</sub>Cu, showing the characteristic peaks of the Soret band of Cu-porphyrin at 410-412 nm,<sup>22</sup> the Q band at 543 nm,<sup>22</sup> and a broad absorption in the 600-700 nm range corresponding to the intracluster charge transfer (ICCT) of the Ru<sub>3</sub> complex moieties in **1-Ru<sub>12</sub>Cu<sup>23</sup>** (Fig. 1(A)). The Ru K-edge and Cu K-edge EXAFS curve-fitting analysis also indicated similar local coordination structures for B-Ru<sub>12</sub>Cu and C-Ru<sub>12</sub>Cu (Fig. 1(B) and Fig. S1-S5, Tables S2, S3, ESI<sup>+</sup>). These results suggested that the coordination structure of 1-Ru12Cu was maintained on SiO2 after stacking the SiO2-matrix overlayers (C-Ru12Cu). Similar trends were observed



Fig. 1 (A) (a) UV-vis spectrum of  $1-Ru_{12}Cu$  (in dichloromethane) and DR UV-vis spectra of (b)  $B-Ru_{12}Cu$ , (c)  $C-Ru_{12}Cu$ , and (d) D-RuCu. (B)  $k^3$ -Weighted Ru K-edge EXAFS Fourier transforms ( $k = 30-160 \text{ nm}^{-1}$ ) for  $1-Ru_{12}Cu$ ,  $B-Ru_{12}Cu$ ,  $C-Ru_{12}Cu$ , and D-RuCu measured at 20 K.

for the other  $Ru_{12}$ -M-porphyrin complexes (M = Ni, Zn) (Fig. S1–S8 and Tables S1–S5, ESI†).

Finally, the grafted  $Ru_{12}$ -metalloporphyrin complexes surrounded by the SiO<sub>2</sub>-matrix overlayers were converted into Ru nanoparticles by reduction with H<sub>2</sub>. The structures of the pyridine moieties anchored on SiO<sub>2</sub> and the grafted  $Ru_{12}$ -metalloporphyrin

 
 Table 1
 Catalytic performance of the obtained catalysts in the hydrogenation of acetophenone<sup>a</sup>

			Selectivity <sup>c</sup> (%)		
Entry	Catalyst	Conv. <sup>b</sup> (%)			OH C
1	_	5	n.d.	n.d.	n.d.
2	Α	3	n.d.	n.d.	n.d.
3	1-Ru <sub>12</sub> Cu	7	n.d.	n.d.	n.d.
4	B-Ru <sub>12</sub> Cu	8	n.d.	n.d.	n.d.
5	C-Ru <sub>12</sub> Cu	4	n.d.	n.d.	n.d.
6	D-RuCu	93	69	10	26
7	D-RuNi	13	45	36	11
8	D-RuZn	40	65	32	14
9	D-Ru	5	n.d.	n.d.	n.d.
10	D-Cu	3	n.d.	n.d.	n.d.

<sup>*a*</sup> Reaction conditions: Ru =  $1.1 \times 10^{-6}$  mol, Ru/acetophenone/ dodecane (internal standard) = 1/500/250 (molar ratio), 0.18 mol L<sup>-1</sup> of acetophenone in 1,4-dioxane, 363 K, 2.0 MPa of H<sub>2</sub>, 6 h. The amounts of the reactant and products were evaluated by GC and GC-MS using an internal standard method. <sup>*b*</sup> Conversion (%) = (initial amount of acetophenone – residual amount of acetophenone)/(initial amount of acetophenone)  $\times$  100. <sup>*c*</sup> Selectivity (%) = (amount of the product)/(initial amount of acetophenone – residual amount of acetophenone)  $\times$  100. n.d. = not determined due to low conversion.

complex were completely diminished (Fig. 1(A) and Fig. S8, ESI<sup>†</sup>). The catalytic activities of the obtained **D-RuM** nanoparticles in the hydrogenation of acetophenone were then evaluated (Table 1) as a model selective hydrogenation reaction of two or more functional groups and frameworks in the reactant molecule.<sup>1,10,12,13</sup> **D-RuCu** was found to exhibit considerable activity in acetophenone hydrogenation (entry 6: 93% conv. (6 h), TOF = 75 h<sup>-1</sup>) compared with **D-RuNi** (entry 7: 13% conv. (6 h)) and **D-RuZn** (entry 8: 40% conv. (6 h)). The major product over **D-RuCu**, **D-RuNi**, and **D-RuZn** was found to be cyclohexyl methyl ketone, indicating that the aromatic ring was reduced more selectively than C=O, which is unique for acetophenone hydrogenation.<sup>24,25</sup> The heterogeneity test of **D-RuCu** showed that the reaction proceeded on the heterogeneous catalyst not in the solution phase (Fig. S9, ESI<sup>†</sup>).

The aromatic hydrogenation did not proceed over A lacking Ru or over **B-Ru<sub>12</sub>Cu** or **C-Ru<sub>12</sub>Cu** with the Ru<sub>12</sub>–Cu–porphyrin coordination structures (entries 2, 4, and 5), and the **1-Ru<sub>12</sub>Cu** precursor was also inactive toward the aromatic hydrogenation in the homogeneous phase (entry 3). Similarly, lower activities were observed over **D-Ru** and **D-Cu** prepared from **1-Ru<sub>12</sub>** without Cu and Cu(tetraphenyl)porphyrin, respectively (entries 9 and 10). These results demonstrate the unique hydrogenation activity of the **D-RuCu** nanoparticle.

Following the exciting result that the single 3d transitionmetal atom (Cu, Ni, or Zn) in the Ru<sub>12</sub>–M–porphyrin precursor **1-Ru<sub>12</sub>M** exerted a great influence on the hydrogenation performance of the **D-RuM** nanoparticles, the structures of these intriguing compounds were further investigated. The Ru K-edge EXAFS Fourier transforms of **D-RuCu**, **D-RuNi** and **D-RuZn** revealed similar peaks corresponding to the Ru–Ru bonds at 0.265–0.267 nm (Fig. 2(A)), with the coordination numbers estimated to be  $3.4 \pm 0.3$ ,  $3.8 \pm 0.3$ , and  $3.6 \pm 0.8$  for **D-RuCu**, **D-RuNi**, and **D-RuZn**, respectively (Fig. S10 and Table S2, ESI†). These relatively small coordination



Fig. 2 (A) Ru K-edge EXAFS Fourier transforms of **D-RuCu**, **D-RuNi**, **D-RuZn**, **D-Ru**, and Ru powder (measured at 20 K). (B) Normalized Ru K-edge XANES spectra of **D-RuCu**, **D-RuNi**, **D-RuZn**, **D-Ru**, RuO<sub>2</sub>, and Ru powder (measured at 20 K).

numbers of around 4 for the Ru–Ru bond suggested the formation of small nanoparticles on the SiO<sub>2</sub> surface (Fig. 2(A)). The HAADF-STEM images of **D-RuCu**, **D-RuNi**, and **D-RuZn** (Fig. S11, ESI<sup>†</sup>) revealed the existence of small Ru nanoparticles whose diameters are in the 0.8–1.5 nm range. The fact that there were no significant peaks in the X-ray diffraction (XRD) patterns (Fig. S12, ESI<sup>†</sup>) suggests that large Ru particles were not found, which is in agreement with the small CNs of Ru–Ru by Ru-K-edge EXAFS. In particular, the positive peak shift of the Ru  $3p_{3/2}$  XPS peak was observed for **D-RuCu** (Fig. 3(A) and Table S6, ESI<sup>†</sup>) (462.2 eV) compared with metallic Ru species (461.1 eV), supporting the formation of small Ru nanoparticles.<sup>26,27</sup>

Ru–O bonds were observed in Ru K-edge EXAFS Fourier transforms of **D-RuCu**, **D-RuNi**, **D-RuZn**, and **D-Ru** (Fig. S10 and Table S2, ESI†); however, the Ru K-edge XANES of **D-RuCu**, **D-RuNi**, and **D-RuZn** revealed clear differences in the degree of oxidation between them. The Ru K-edge energy, which is relevant to the Ru valence, of **D-RuCu** was the largest (22124 eV), and this value decreased in the order of **D-RuZn** 



Fig. 3 (A) Ru  $3p_{3/2}$  XPS spectra of **D-RuCu** (red), **D-RuNi** (blue), and **D-Ru** (black). (B) Cu 2p XPS spectra of **D-RuCu**. (C) Ni 2p XPS spectra of **D-RuNi**. The intensities of the spectra were normalized using the Si 2p XPS peak area.

(22123 eV), **D-RuNi** (22121 eV), and **D-Ru** (22118 eV) (Fig. 2(B)). These results indicate that **D-RuCu** was the most oxidized (or the most positively charged) relative to **D-RuZn**, **D-RuNi**, and **D-Ru**. The positive shift of the Ru  $3p_{3/2}$  XPS peak of **D-RuCu** (462.2 eV) compared with **D-RuNi** (461.5 eV) (Fig. 3(A) and Table S6, ESI†) is in agreement with the Ru K-edge XANES results. Thus, the Ru nanoparticles in **D-RuCu** were more positively charged Ru species than those in other **D**-series.

The Cu, Ni and Zn K-edge XANES showed that Cu, Ni, and Zn species were not reduced to zero-valent (Fig. S13–S15, ESI†), and the Cu, Ni and Zn K-edge EXAFS Fourier transforms suggested the existence of Cu–O, Ni–O, and Zn–O coordination (Fig. S13–15 and Tables S3–S5, ESI†). The Ni 2p XPS peaks of **D-RuNi** were observed at 860.9 eV (Ni  $2p_{3/2}$ ) and 880.9 eV (Ni  $2p_{1/2}$ ) (Fig. 3(C)), whereas the Cu 2p XPS peak of **D-RuCu** was too weak to be observed (Fig. 3(B)). These results indicated that the oxidized Cu species in **D-RuCu** were not located at the catalyst surface but might be instead covered by Ru species (Scheme 1). In contrast, the oxidized Ni species might be located at the SiO<sub>2</sub> surface and not be covered by the Ru nanoparticles or SiO<sub>2</sub>-matrix overlayers (Scheme 1).

Based on the above discussion from surface characterization results, a raft-like Ru nanostructure is plausible on the SiO<sub>2</sub> surface, leading to an increase in the Ru valence by positive interaction with the oxide surface, as illustrated in Scheme 1. The most oxidized Ru nanostructures at the surface of **D-RuCu** compared with other Ru nanoparticles of **D-RuNi**, **D-RuZn**, and **D-Ru** would provide electron-deficient reaction sites, which are favorable for interactions with the electron-rich aromatic rings of acetophenone.<sup>28</sup> The present study suggests the possibility of the selective transformation of novel metal nanostructures using single 3d transition metals, leading to improvements in their catalytic performance.

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## Conflicts of interest

There are no conflicts to declare.

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