Electronic Interactions between Stable Electride and Nano-alloy Control the Chemoselective Reduction Reaction

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Methods

Preparation of Ru-Fe/C12A7:e−
C12A7:e− electrode powders were prepared by the reaction of C12A7, CaO·Al₂O₃ (CA) and Ca metal at 1100 °C. Ru and Fe loading was conducted by chemical vapor deposition (CVD) process using their corresponding metal carbonyl Ru₃(CO)₁₂ and Fe₉(CO)₁₉ precursors. In a typical catalyst synthesis, C12A7:e− electrode powders with Ru₃(CO)₁₂ and Fe₉(CO)₁₉ were sealed in an evacuated silica tube and heated under a temperature program as shown in Fig. S1.

Hydrogenation of α,β-unsaturated aldehydes
All reactions were carried out in a 25-mL stainless steel autoclave fitted with a glass mantel, 60-bar manometer, and a magnetic stirrer. In a typical reaction, 100 mg of catalyst and 8 mmol substrates were sealed in the autoclave. Then autoclave was flushed three times with H₂, pressurized with H₂ (20 bar), and heated to 130 °C over 30 min with stirring (800 rpm). The reactor was held at this temperature for 12 h. The products were analyzed by gas chromatography (GC) with an external standard of benzyl alcohol and the identity of the products was further confirmed by GC-MS.

Characterization.
Samples for examination by scanning transmission electron microscopy (STEM) were prepared by dispersing the dry catalyst powder onto a holey carbon film supported by a 300 mesh copper TEM grid. STEM high angle annular dark field (HAADF) images of the supported metal nanoparticles were obtained using an aberration corrected JEM ARM-200 F STEM operating at 200 kV. X-ray energy dispersive (XEDS) spectra were acquired from individual metal nanoparticles 41 nm in size by rastering the beam over the entire metal particle, while using a JEOL Centurio 0.9sr silicon drift detector. The sample powders were also dispersed onto an Al-stub and examined in SE and backscatter mode in a JEOL JSM-7600F scanning electron microscope (SEM) equipped with an EDAX energy dispersive X-ray spectrometer. Transmission electron microscopy (TEM) measurements were conducted in bright field imaging mode using a Tecnai 20FEG transmission electron microscope operating at 200 kV. The mean Ru particle diameters were calculated by determining the size of more than 200 particles per sample using iTEm software (soft Imaging System GmbH).

X-ray photoelectron spectroscopy (XPS, ESCA-3200, Shimadzu) measurements were carried out using Mg Ka radiation at < 10⁻⁶ Pa (applied bias voltage to X-ray source of 8 kV).

The Brunauer–Emmett–Teller specific surface areas of the samples were determined by the measurement of nitrogen adsorption–desorption isotherms at −196 °C using an automatic gas-adsorption instrument (BELSORP-mini II, MicrotracBEL) after evacuation of the samples at 150 °C. Ru content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; ICPS-8100, Shimadzu).
H$_2$-temperature-programmed reduction (H$_2$-TPR) profiles were measured in a BELCAT-A instrument (MiccrotracBEL, Japan). A 500 mg samples were pretreated in O$_2$ (30 mL/min) at 623 K for 30 min to remove CO adsorbed on the surface and then cooled to room temperature. Subsequently, reducing gas composed of 5% H$_2$/95% Ar was employed at a flow rate of 30 mL/min and a heating rate of 10 K/min from ambient to 1173 K. The consumption of H$_2$ was monitored by a thermal conductivity detector (TCD) and mass spectrometer (Bell Mass, MiccrotracBEL, Japan). To investigate the oxidation and reduction of the bimetallic system during the H$_2$-TPR characterization, we investigated the structure of 5wt%Ru-5wt%Fe/SiO$_2$ by XRD analysis after the pretreatment the same as Ru-Fe/C12A7:e$^-$ and re-reduction in 5% H$_2$/95% Ar, respectively (Fig. S12).

FT-IR spectra of adsorbed CO were measured using a spectrometer (FT/IR-6100, Jasco) equipped with a mercury–cadmium–tellurium detector at a resolution of 4 cm$^{-1}$. Samples were pressed into self-supported disks. A disk was placed in a silica-glass cell equipped with KBr windows and connected to a closed gas-circulation system to allow thermal adsorption–desorption experiments. The disk was pretreated with circulated H$_2$ at 350 °C for 2 hours and then cooled to room temperature. After the pretreatment, the disk was cooled to −170°C under vacuum to obtain a background spectrum. Pure CO (99.999999%) were supplied to the system through a liquid-nitrogen trap. The infrared spectrum of the sample at −170°C prior to CO adsorption was used as the background for difference spectra obtained by subtracting the backgrounds from the spectra of CO-adsorbed samples.
Fig. S1 Detailed synthetic parameters for preparing Ru-Fe/C12A7:e−.
Heated temperature program: 2 °C min⁻¹ up to 40 °C, held for one hour, 0.25 °C min⁻¹ up to 70 °C, held for one hour, 0.4 °C min⁻¹ up to 120 °C, held for one hour, 0.9 °C min⁻¹ up to 250 °C, held for two hours and then cooled to ambient temperature. The all program was operated under vacuum.
**Fig. S2** XRD patterns of pure C12A7:e− and Ru-Fe/C12A7:e−. The bottom green columns and orange columns represent the reference XRD patterns of Fe (JCPDS No.65-4899) and Ru (JCPDS No.65-1863) metal.
Fig. S3 XRD patterns of 5wt%Ru-5wt%Fe/SiO$_2$. The bottom blue columns represent the reference XRD patterns of RuFe (JCPDS No.65-6545).

We loaded 5wt%Ru-5wt%Fe onto the surface of amorphous SiO$_2$ under the same preparation condition as Ru-Fe/C12A7:$\cdot e^-$. As we expected, the RuFe alloy with a hexagonal close-packed phase (space group: P63/mmc, JCPDS No. 65-6545) is formed on the support.
**Fig. S4** XPS Ru 3p (a) and Fe 2p (b) spectra for Ru-Fe/C12A7:e−. The dotted lines indicate the Ru 3p and Fe 2p peaks derived from bulk Ru and Fe metal respectively.
Fig. S5 SEM images of Ru-Fe/C12A7:e− surface: overview (a) and enlargement of a homogeneous section (b) from (a). Inset (b): Metallic particle size distribution.
Table S1. Summary of reported Ru, Pt and other transition metal based heterogeneous catalysts for hydrogenation of cinnamaldehyde.

| Catalyst                  | Solvent      | B.E.T. [m²g⁻¹] | Conv. [%] | Sel. [%] | Ref.     |
|---------------------------|--------------|----------------|-----------|----------|----------|
| Ru-Fe/C12A7:e             |              | 0.8            | 96.2      | 96.7     | This work|
| Ru/CNT                    | isopropanol  | 27             | 80        | 92       | [S1]     |
| Ru-Sn/SiO₂                | isopropanol  | 297            | 99        | 59       | [S2]     |
| Pt-Ru/CNT1273             | dioxane      | 246            | 78        | 94       | [S3]     |
| 2% Pt 2% Ru/MWNT          | isopropanol  | 196            | 79        | 93       | [S4]     |
| Ru/HSAG@mSiO₂             | isopropanol  | 613            | 95        | 65       | [S5]     |
| Pt(2.41%)/LDH-EG          | ethanol      | 87.8           | 93.6      | 78.8     | [S6]     |
| 3.5 wt%Pt/C              | isopropanol  | 57             | 92        | 88       | [S7]     |
| Pt(5.0%)/C12A7            | ethyl acetate (EAS) | 23            | 89.8      | 78.8     | [S8]     |
| 0.3%Pt–0.1%Co/ZrO₂        | ethanol      | 74.8           | 90.2      | 88.0     | [S9]     |
| 0.5%Pt–0.17%Co/CNT        | ethanol      | 110            | 92.4      | 93.6     | [S10]    |
| PtCo/0.5-CNx/TiO₂         | ethanol      | Unknown        | 97.1      | 79.3     | [S11]    |
| Pt(5%)/CeO₂–ZrO₂          | isopropanol  | 94             | 95.8      | 93.4     | [S12]    |
| Pt(1.96%)/MA              | water        | Unknown        | 79.7      | 85.4     | [S13]    |
| PtNCs/UiO-66-NH₂          | methanol     | 676            | 98.7      | 91.7     | [S14]    |
| Pt/RGO                   | isopropanol  | 276.1          | 89.6      | 69.6     | [S15]    |
| Pt-Co/Graphene            | isopropanol  | Unknown        | 94.6      | 89.5     | [S16]    |
| Pt/RGO                   | ethanol      | 343.2          | 97.8      | 85.3     | [S17]    |
| PtFeZn/C-UA               | cyclohexane  | 800            | 96        | 86       | [S18]    |
| Pd–Sn/AC                  | isopropanol  | Unknown        | 96        | 80       | [S19]    |
| Au/BP (Au; 1.1 mol%)      | water        | 107            | 78        | 80       | [S20]    |
| Au–Ir/TiO₂                | isopropanol  | 50             | 95        | 75       | [S21]    |
| AuNPs/TiO₂/reduced        | isopropanol  | 60             | 61.6      | 49.3     | [S22]    |
| Ni/TiO₂                  | methanol     | 150            | 91.0      | 61.0     | [S23]    |

*Electrochemical active surface (EAS) areas of Pt nanoparticles by using CO stripping method.
| Entry | Catalyst       | Ru : Fe [wt%] | H₂ [MPa] | Temp. [°C] | Time [h] | Conv. [%] | Sel. [%] |
|-------|----------------|---------------|----------|------------|---------|-----------|----------|
| 1     | Ru-Fe/C12A7:e⁻ | 1:1           | 1.0      | 130        | 12      | 33.3      | 87.1     |
| 2     | Ru-Fe/C12A7:e⁻ | 1:1           | 2.0      | 110        | 12      | 40.5      | 92.6     |
| 3     | Ru-Fe/C12A7:e⁻ | 1:1           | 2.0      | 90         | 12      | 20.2      | 92.5     |
| 4     | Ru-Fe/C12A7:e⁻ | 1:1           | 2.0      | 60         | 72      | 20.4      | 94.5     |
| 5     | Ru-Fe/C12A7:e⁻ | 1:1           | 2.0      | 130        | 6       | 21.4      | 93.3     |
| 6     | Ru-Fe/C12A7:e⁻ | 1:1           | 2.0      | 130        | 12      | ----      | ----      |
| 7     | Ru-Fe/C12A7:e⁻ | 2.5:2.5       | 2.0      | 130        | 12      | 96.9      | 85.6     |
| 8     | Ru-Fe/C12A7:e⁻ | 5:5           | 2.0      | 130        | 12      | 98.6      | 80.7     |
| 9     | Ru-Fe/C12A7:e⁻ | 2:1           | 2.0      | 130        | 12      | 98.1      | 76.6     |
| 10    | Ru-Fe/C12A7:e⁻ | 10:1          | 2.0      | 130        | 12      | 98.0      | ----      |
| 11    | Ru-Fe/C12A7:e⁻ | 1:1           | 2.0      | 130        | 12      | 91.2      | 79.6     |
| 12    | Ru-Fe/C12A7:e⁻ | 1:1           | 2.0      | 130        | 12      | 93.4      | 91.3     |

*Typical conditions: 8 mmol cinnamaldehyde, 100 mg of catalyst;*  
*Substrate: 8mmol cinnamyl alcohol, 100 mg of catalyst;*  
*C12A7:e⁻ with $N_e = 1.2 \times 10^{20}$ cm$^{-3}$;*  
*C12A7:e⁻ with $N_e = 1.1 \times 10^{21}$ cm$^{-3}$.*
Fig. S6 SEM images of several bimetallic Ru-Fe/C12A7:e− catalysts with different Ru/Fe weight ratios: (a) 1wt%Ru-1wt%Fe/C12A7:e−, (b) 2.5wt%Ru-2.5wt%Fe/C12A7:e− and (c) 5wt%Ru-5wt%Fe/C12A7:e−. Inset: Metallic particle size distribution.

We appropriately tune of Ru-Fe loading amount from 2 wt% to 10 wt%, the mean size of the metal nanoparticles was increased from 15 to 20 nm with metal nanoparticles aggregated gradually. Accordingly, the selectivity to cinnamyl alcohol decreased a lot although the conversion slightly elevated (Table 1, entry 4; Table S2, entries 7–8). The larger nanoparticles aggregation would decrease the fraction of metal-support interface, reducing the selectivity to cinnamyl alcohol.
Fig. S7 SEM images of several bimetallic Ru-Fe/C12A7:e⁻ catalysts with different Ru/Fe weight ratios: (a) 2wt%Ru-1wt%Fe/C12A7:e⁻, (b) 10wt%Ru-1wt%Fe/C12A7:e⁻.

When Ru-rich catalyst were used (Table S2, entries 9–10), the selectivity decreased sharply, attributed to the superabundant of active metal Ru which can be clearly observed on the surface morphology of the catalyst.
Fig. S8 The UV-vis absorption spectra (obtained by Kubelka-Munk transformation of diffuse reflectance spectra) for the synthesized powders of C12A7:e\(^{-}\) or C12A7:O\(^{2-}\) with various electron concentrations (a) \(N_{e} = 2.2 \times 10^{21} \text{ cm}^{-3}\), (b) \(N_{e} = 1.1 \times 10^{21} \text{ cm}^{-3}\), (c) \(N_{e} = 1.2 \times 10^{20} \text{ cm}^{-3}\), (d) \(N_{e} = 0 \text{ cm}^{-3}\).
\[ N_e = 2.2 \times 10^{21} \text{ cm}^{-3} \quad N_e = 1.1 \times 10^{21} \text{ cm}^{-3} \quad N_e = 1.2 \times 10^{20} \text{ cm}^{-3} \quad N_e = 0 \text{ cm}^{-3} \]

**Fig. S9** The photographs of the synthesized powders of C12A7:e\(^-\) or C12A7:O\(^2-\) with various electron concentrations.

The sample color was changed from white by green to black when \( N_e \) increased from 0 to \( 2.2 \times 10^{21} \text{ cm}^{-3} \), which is good agreement with the colors of C12A7 single crystals treated with Ca metal in a vacuum. There is no adsorption peak of C12A7:O\(^2-\) sample in the visible region, and the corresponding 3.5 eV absorption edge is attributed to the excitation between the energy level of encaged O\(^2-\) ions and the cage conduction band (CCB). By contrast, C12A7:e\(^-\) samples give broad absorption bands at 2–3.5 eV and below 2 eV. The former absorption is due to an intracage s-to-p transition of electrons trapped in the cages, and the latter is attributed to an intercage s-to-s transition as charge transfer from an electron-trapped cage to a vacant neighboring cage. The absorption band below 2 eV is broadened, and the band tail extends to larger energies, which is affected by the disorder of the extra framework species. It was therefore confirmed that O\(^2-\) ions accommodated in the cages of C12A7:O\(^2-\) are replaced by electrons by heat treatment with Ca metal in a vacuum.
Table S3. Electron Concentration ($N_e$) of C12A7:e$^-$ or C12A7:O$^{2-}$ samples.

| $N_e^a$ ($10^{21}$cm$^{-3}$) | $N_e^b$ ($10^{21}$cm$^{-3}$) |
|-------------------------------|-------------------------------|
| 2.2                          | 2.1                          |
| 1.1                          | 1.5                          |
| 0.12                         | 0.10                         |
| 0                            | 0                            |

$N_e^a$ was determined by iodometric titration method. $N_e^b$ was determined by the relation of $N_e = [- (E_{sp} - E_{sp}^o)/0.199]^{0.782}$.

$N_e$ can be estimated from $E_{sp}$ using the experimentally obtained relation of $N_e = [- (E_{sp} - E_{sp}^o)/0.199]^{0.782}$, where the low-$N_e$ limit $E_{sp}^o = 2.83$ eV at $N_e \approx 1 \times 10^{18}$ cm$^{-3}$. The obtained values correspond well with those determined by the iodometric titration method.
Table S4 Chemoselective hydrogenation of benzalacetone using Ru-Fe/C12A7.e. 

| Entry | Substrate | Product | Conv. [%] | Sel. [%] |
|-------|-----------|---------|-----------|---------|
| 1     | ![Substrate](image1) | ![Product](image2) | 42.2      | 15.1    |

* Typical conditions: 8 mmol substrate, 100 mg catalyst, H₂ (2.0 MPa), 90 °C, 24 h.

In the case of chemoselective reduction of α,β-unsaturated ketone, we tried the hydrogenation of benzalacetone under solvent free system and the conversion and selectivity was quite poor compared with cinnamaldehyde (entry 1). Probably, the steric hindrance by the methyl group in α,β-unsaturated ketone impeded adsorption of the C=O bonds to the Ru-Fe active sites significantly.
Fig. S10 Difference DRIFTS spectrum of CO molecules adsorption on Fe/C12A7:O$^{2-}$ at −170 °C under 5 KPa of CO.
Fig. S11 Effect of substrate concentration on the rates of hydrogenation of cinnamaldehyde (Catalyst: 5 mg; THF: 5 mL; 2MPa H$_2$, 130 °C; 12h).
Fig. S12 XRD patterns of (a) 5wt%Ru-5wt%Fe/SiO\textsubscript{2} pretreated in O\textsubscript{2} (30 mL/min) at 623 K for 30 min; 5wt%Ru-5wt%Fe/SiO\textsubscript{2} re-reduction in H\textsubscript{2}/Ar (30 mL/min) at 623 K for 30 min. The bottom blue, green and orange columns represent the standard JCPDS diffraction pattern of RuFe (JCPDS No.65-6545), RuO\textsubscript{2} (JCPDS No.40-1290), and Fe\textsubscript{2}O\textsubscript{3} (JCPDS No.39-1346), respectively.

We measured the XRD pattern of 5wt%Ru-5wt%Fe/SiO\textsubscript{2} with oxidation treatment, which is the same as the pretreatment of H\textsubscript{2}-TPR (O\textsubscript{2}, 623 K, 30 mins). Part of the hexagonal RuFe alloy phase remained and RuO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} phases were also observed in the XRD pattern (Fig. R1a). Although phase separation between Ru oxide and Fe oxide occurred during the oxidation pretreatment, the re-reduction process brought about the RuFe alloy formation again (Fig. R1b). Therefore, we think that RuO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} are present in close proximity to each other on the surface of the RuFe alloy after the oxidation treatment. As a result, H\textsubscript{2}-TPR peaks for Ru-Fe catalysts are observed in the intermediate temperature region between that of Ru and Fe catalysts (Fig. 3a).
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